PRACTICAL CHEMISTRY

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PRACTICAL CHEMISTRY

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BY

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PREFACE.

THIS little book provides a course of experimental work which is designed to meet the requirements of the Senior Cambridge Local Examination in Practical Chemistry.

It is divided into three parts. In Part I., Chapter I., a number of carefully selected preparations are described, with full working details and diagrams (where necessary); in Chapter II. the action of heat on some typical substances is investigated. Part II. deals with Quantitative Analysis, Chapter I. consisting of a selection of simple experiments mainly gravimetric, whilst Chapter II. contains an elementary treatment of Volumetric Analysis. Part III. is concerned with the Qualitative Analysis of Simple Salts. The syllabus of the Examination, however, states that alternative questions will be set, so that a candidate may avoid the Qualitative Analysis altogether if he wishes.

No apologies are needed for writing a text-book to a particular syllabus provided it is a good syllabus. As this condition is certainly satisfied the author hopes that the book will be found useful by a wider range of students than those for whom he is ostensibly writing.

We have to thank the Controller of His Majesty's Stationery Office, and also Messrs. Macmillan and Co. for their kind permission to include in this book the Tables of Logarithms and Antilogarithms published in "Examinations in Science and Technology."

H. W. BAUSOR.

CAMBRIDGE
September 1918.

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PART I.

CHAPTER I.

PREPARATIONS.

In the following pages the working details of a number of preparations are described. If the student is to obtain satisfactory results it is all-important that he should carry out these details *exactly*. Careful notes of each preparation should be made at the time of the experiment, accompanied in general by a sketch of the apparatus used. Following a preparation the student is usually directed to carry out some experiments with the substance prepared, in order to identify it or to test its purity. Precise notes of the results of these experiments should also be made.

1. Hydrogen Peroxide, H_2O_2.—Add 10 c.c. of concentrated sulphuric acid, gradually with stirring, to 200 c.c. of water, and allow the mixture to stand till it becomes quite cold; now add little by little, with constant stirring, about 30 grams of barium dioxide. Allow to settle, and decant off the clear liquid, which is a dilute solution of hydrogen peroxide. The change which takes place is represented by the equation

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

The following experiments should be performed with the solution:—

(1) To some of the liquid add a little potassium iodide solution; iodine will be liberated, and the solution become brown.

$$2KI + H_2O_2 = 2KOH + I_2.$$

(2) Make a dark stain of sulphide of lead on filter paper by first moistening it with a solution of a lead salt,

say the acetate, and then exposing this to sulphuretted hydrogen gas (or dipping it in an aqueous solution of the gas). Steep the paper in a little of the hydrogen peroxide solution and it will become white, the black sulphide of lead having been transformed into the white sulphate, as shown in the following equation:—

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$

(3) Add silver nitrate to some of the solution, and then caustic soda. A black precipitate of hydrated oxide of silver will be formed, and this in contact with the hydrogen peroxide will undergo decomposition with effervescence of gas, which may be shown to be oxygen by testing with a glowing splint.

$$2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O.$$
$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

2. Aqueous Hydrochloric Acid.—This preparation may conveniently be carried out in the apparatus represented in Fig. 1. The flask should have a capacity of about $\frac{3}{4}$ litre; that of the beaker should be about 200 c.c. Introduce about 30 grams of common salt into the flask and fill the beaker about one third full of distilled water. Now connect up the apparatus as shown, arranging so that the rim of the funnel dips *just below** the surface of the water in the beaker. The limb of the delivery tube to which the funnel is attached should be supported by means of a retort stand and clamp (not shown in the diagram).

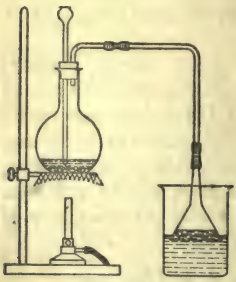

Fig. 1.

Next prepare a small quantity of somewhat dilute sulphuric acid† by pouring 35 c.c. of concentrated sulphuric

* An alternative arrangement consists in having the rim of the funnel *just above* the surface of the water.

† The use of a somewhat dilute acid avoids excessive frothing.

acid gradually into a flask containing 25 c.c. of water, shaking after each addition. Cool the acid by holding the flask under the tap, and then pour a little of it down the thistle funnel. Hydrogen chloride is evolved with effervescence, and, owing to its great solubility, is completely absorbed by the water in the beaker. The change which takes place is represented by the equation

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

When the reaction slackens add a little more of the acid, and so on till the whole has been run in. Finally warm the flask gently with a Bunsen burner in order to complete the reaction. The liquid in the beaker now consists of *concentrated hydrochloric acid* and smells strongly of the gas.

The arrangement adopted for the absorption of the gas prevents the possibility of the liquid in the beaker "sucking back" into the generating flask, owing to the great solubility of the gas; for as soon as the solution has risen a little way up the funnel, the level of liquid in the beaker falls to that of the rim of the funnel.

The action of the acid solution on litmus paper and on a solution of silver nitrate should be tested; also its action on metals such as iron, zinc, and copper, and on manganese dioxide and red lead.

3. Pure Sodium Chloride, NaCl.—Prepare a cold saturated solution of common salt and pass into it a stream of hydrogen chloride prepared as in the previous experiment (using the same absorption apparatus). Crystals of sodium chloride soon begin to separate out of solution. When a sufficient quantity have collected they should be filtered off, washed with a little pure concentrated hydrochloric acid, and allowed to dry in the air (or by gently warming in a dish). Introduce the specimen into a wide-mouthed * bottle of suitable size provided with a glass stopper or well-fitting cork, and label it.

* *Wide-mouthed* bottles should be used for *solids*, narrow-mouthed for liquids.

4. Aqueous Hydrobromic Acid.—This may conveniently be prepared by passing sulphuretted hydrogen into bromine water, when the following change takes place:—

$$2H_2S + 5Br_2 + 4H_2O = 10HBr + H_2SO_4 + S.$$

Introduce a few pieces of ferrous sulphide into a flask fitted with a thistle funnel and delivery tube. Pour dilute sulphuric acid down the funnel and pass the sulphuretted hydrogen which is evolved into some bromine water contained in a small flask. Note that the reddish brown colour of the solution gradually disappears and a precipitate of sulphur is formed. This should be filtered off.

The presence of hydrobromic acid in the filtered solution should be proved by adding a solution of silver nitrate, when a yellowish white precipitate of silver bromide, AgBr, is formed.

$$AgNO_3 + HBr = AgBr + HNO_3.$$

5. Iodine, I_2.—Introduce into a tubulated retort a mixture of about 20 grams of potassium iodide and 10 grams of manganese dioxide. Cover the mixture with strong sulphuric acid poured in through a funnel inserted in the tubulus of the retort. Insert the stopper and place over the open end of the retort a flask resting in a trough of water.

Heat the mixture gently. Iodine distils over and condenses as a blue-black solid, partly in the receiver and partly in the neck of the retort; that in the latter can be driven into the receiver by gently warming with a Bunsen burner. The change which takes place is represented by the equation

$$2KI + 3H_2SO_4 + MnO_2 = 2KHSO_4 + MnSO_4 + 2H_2O + I_2.$$

Bottle the specimen and label it.

Test the solubility of the specimen in water, potassium iodide solution, alcohol, carbon disulphide, and benzene, noting the colour of the solution in each case.

6. Hydrogen Iodide, HI.—Fit up the apparatus shown in Fig. 2,* using a flask of about ½ litre capacity. Fill the U-tube with lumps of red phosphorus. Introduce into the flask 1 gm. of powdered red phosphorus and 20 gm. of iodine. Pour 10 c.c. of water into the funnel and run it *gradually* into the flask. Hydrogen iodide is evolved *without heating*, and, after being purified by the phosphorus in the U-tube (which removes iodine vapour), is collected in *dry* jars by downward displacement.

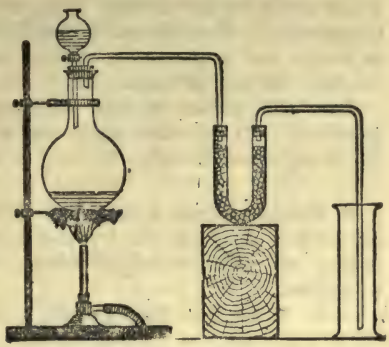

Fig. 2.

When the gas fumes strongly at the mouth of the jar you may assume that the latter is full of gas. Remove it, cover its mouth with a glass plate greased with a little vaseline, and place another in position.

When all the water has been run into the flask and the evolution of gas becomes slow, warm gently by means of a Bunsen burner to complete the reaction, which is represented by the equation

$$P_4 + 10I_2 + 16H_2O = \underset{\text{Phosphoric acid}}{4H_3PO_4} + 20HI.$$

Show that the gas is not combustible and does not support combustion, that it is acid to moist litmus, and that it is very soluble in water (invert a jar in water). Also pour some chlorine water into a jar of the gas and note the separation of iodine.

$$2HI + Cl_2 = 2HCl + I_2.$$

* The delivery tube leading from the U-tube to the jar should be in two parts joined by rubber tubing, so that the jar can be replaced by others as required.

7. Aqueous Hydriodic Acid.—The same apparatus is used as in the last preparation, except that an absorption apparatus similar to that used in the preparation of aqueous hydrochloric acid (Preparation 2) is attached to the U-tube. Use the same quantities of reacting materials as in the last preparation, and collect the hydrogen iodide in about 50 c.c. of water.

Test the action of the solution on (1) silver nitrate solution, (2) metals such as zinc, iron, and copper, (3) manganese dioxide.

8. Nitrogen from Ammonia.—The method to be adopted consists in oxidising the hydrogen of ammonia to water by means of red-hot copper oxide, thus setting free the nitrogen.

$$3CuO + 2NH_3 = N_2 + 3H_2O + 3Cu.$$

We shall so arrange the experiment as to show that water as well as nitrogen is formed, thus incidentally proving that ammonia contains the elements *nitrogen* and *hydrogen*.

Take a piece of hard glass tubing about 50 cm. long and fit it with a one-holed cork at each end. Through one cork pass a short piece of straight glass tubing and through

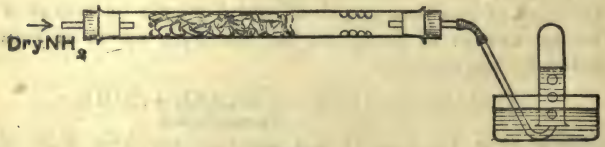

Fig. 3.

the other a delivery tube for collecting gas over water. Partly fill the tube with dry granulated copper oxide, leaving a space of about 15 cm. empty at the end to which the delivery tube is attached (Fig. 3). Now attach the straight tube to an apparatus for preparing dry ammonia. This consists of a small round-bottomed flask containing a mixture of 10 gm. of sal-ammoniac and

20 gm. of slaked lime, to which is attached a **U**-tube filled with lumps of quicklime or soda lime to dry the gas.

Support the long tube horizontally in a clamp, and place the delivery tube under water. Heat the copper oxide red-hot by a flat-flame burner; then warm the ammonia generator.

After the reaction has been going on long enough for the expulsion of air from the apparatus, collect some of the gas which is given off, and show that it is *nitrogen* by the usual tests. The colourless drops of liquid which collect in the cool part of the tube may be shown to be *water* in the usual way.

9. Lead Nitrate and Liquid Nitrogen Peroxide.

(*a*) *Lead Nitrate*, $Pb(NO_3)_2$.—Pour about 10 c.c. of dilute nitric acid into a small flask, add 6 gm. of metallic lead in small fragments, and warm on a water-bath in the fume cupboard. If all the metal dissolves add a few

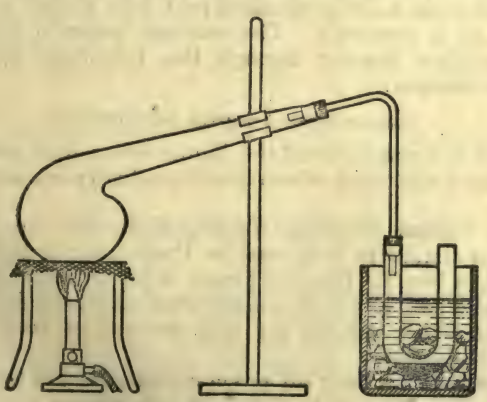

Fig. 4.

more fragments, and repeat this till no more will dissolve. Filter into a porcelain dish and evaporate to dryness on the water bath. The white residue is lead nitrate.

(*b*) *Liquid Nitrogen Peroxide*, N_2O_4.—Powder up finely the lead nitrate you have just prepared and introduce it into a hard glass retort. Connect this with a **U**-tube immersed in a freezing mixture of pounded ice and salt contained in a deep trough—see Fig. 4 (a jam jar will serve the purpose). Heat the retort strongly. The lead nitrate melts and then brown fumes of nitrogen peroxide are given off and condense in the **U**-tube to a colourless liquid.

$$2Pb(NO_3)_2 = 2PbO + 2N_2O_4 + O_2.$$

The lead oxide formed remains behind as a brownish-red solid, which becomes yellow on cooling. [If the temperature used is sufficiently high the oxide melts, forming a *red liquid*.]

When the decomposition appears to be complete remove the freezing mixture, and note that as the temperature rises the liquid darkens in colour, and at ordinary temperatures is *orange yellow*.

Now pour a little of the liquid into a dish and add water to it gradually. The nitrogen peroxide dissolves, the solution passing through the following series of colour changes :—

Blue→green→orange→colourless.

Pour the remainder of the liquid into a dish and leave in a fume cupboard, where it will gradually evaporate.*

10. Sodium Sulphite, $Na_2SO_3.7H_2O$.—Fit up an apparatus similar to that used in Preparation 2 and represented in Fig. 1. Place 10 grams of copper turnings in the flask and add 40 c.c. of concentrated sulphuric acid. Introduce 50 c.c. of a ten per cent. solution of caustic soda into the beaker.

Now heat the flask till action commences and then turn the burner down so that it does not become too violent. The sulphur dioxide which is evolved is absorbed by the caustic soda, and the solution finally becomes *apple green*

* If it were to be preserved it would be introduced into a glass tube, which would then be sealed off.

in colour and *smells strongly* of the gas. When this is the case you have a solution of sodium hydrogen sulphite, $NaHSO_3$.

Now discontinue passing sulphur dioxide through the liquid and add to it another 50 c.c. of the caustic soda solution (*i.e.* a volume equal to that you used at first): this converts the acid sulphite into the normal salt. Allow the solution to stand, when colourless crystals having the composition $Na_2SO_3 . 7H_2O$ will separate out. These should be filtered off, washed with a little cold distilled water, and dried between folds of blotting-paper. They may be preserved in a small stoppered bottle.

The reactions which take place are represented by the following equations:—

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$
$$NaOH + SO_2 = NaHSO_3.$$
$$NaHSO_3 + NaOH = Na_2SO_3 + H_2O.$$

Show that the salt is decomposed by a dilute acid (*e.g.* sulphuric) with evolution of sulphur dioxide, recognised by its odour.

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

11. Sulphur Trioxide, SO_3.—This compound is conveniently prepared by distilling concentrated sulphuric acid with phosphoric oxide, the reaction being thus represented—

$$P_4O_{10} + 2H_2SO_4 = \underset{\text{Metaphosphoric acid}}{2H_2P_2O_6} + 2SO_3.$$

Owing to the very hygroscopic nature of the reagents and the product, it is important that the vessels used should be *quite dry*. Therefore dry a small tubulated retort and a flask by warming them over a Bunsen flame, driving a current of air through them by a glass tube attached to a foot bellows.

Introduce into the retort about 10 grams of concentrated sulphuric acid and add gradually 15 grams of phosphoric oxide. Place the flask over the mouth of the retort, arranging so that it dips in a trough of water

containing some pieces of ice (Fig. 5), and cover it with a wet cloth. Warm the retort gently. Sulphur trioxide distils over, and condenses in the receiver in the form of white silky needles.

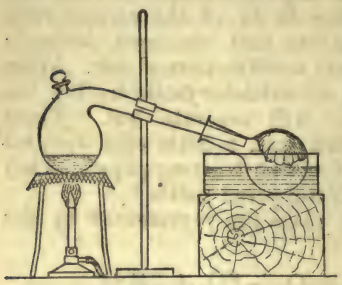

Fig. 5.

Drop a *small* quantity of the crystals into a little water in a beaker and note the hissing sound with which they dissolve; also note that the beaker becomes warm. Show that the liquid now contains sulphuric acid by adding a solution of barium nitrate, $Ba(NO_3)_2$, when a white precipitate of barium sulphate, $BaSO_4$, is formed.

$$SO_3 + H_2O = H_2SO_4.$$
$$H_2SO_4 + Ba(NO_3)_2 = BaSO_4 + 2HNO_3.$$

The remainder of the crystals may be preserved in a well-stoppered bottle.

12. Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$. — Dissolve some crystallised sodium sulphite almost to saturation, in water, in a flask; add flowers of sulphur a little at a time till some remains undissolved, even on heating. Filter off the excess of sulphur and allow the filtrate to cool. Filter off the crystals which separate out, wash them with a little distilled water, and dry them by pressing between filter paper.

The change which takes place is represented by the equation

$$Na_2SO_3 + S = Na_2S_2O_3.$$

Dissolve a little of the salt in water and add dilute sulphuric acid. Note the formation of a precipitate of sulphur and the odour of sulphur dioxide.

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2 + S.$$

13. Phosphoric Acid, H_3PO_4.—Introduce about 10 grams of red phosphorus into a large retort and cover it with concentrated nitric acid. Warm gently in a fume cupboard. The phosphorus gradually dissolves, and red fumes of nitrogen peroxide are evolved. The change which takes place may be represented by the equation

$$2P + 10HNO_3 = 2H_3PO_4 + 10NO_2 + 2H_2O.$$

When all the phosphorus has disappeared transfer the liquid to a porcelain dish and evaporate to small bulk. Add a little more nitric acid and again evaporate. Repeat this operation till no brown fumes are produced on evaporation, showing that all the phosphorous acid, H_3PO_3, which is formed at first to some extent has been oxidised to phosphoric acid. Continue the last evaporation till acid fumes (nitric acid) ceases to be evolved. Allow the thick residue to stand in a cool place: colourless crystals will separate after a time.

14. Microcosmic Salt, $NaH(NH_4)PO_4.4H_2O$. — Dissolve 36 grams of the common sodium phosphate, $Na_2HPO_4.12H_2O$, in as small a quantity of hot water as possible, and add 6 grams of ammonium chloride dissolved in a small volume of water. Leave the solution to cool: crystals of microcosmic salt separate out. These should be filtered off, washed with a little cold water, and dried between several folds of filter paper.

The reaction is thus represented—

$$Na_2HPO_4 + NH_4Cl = NaH(NH_4)PO_4 + NaCl.$$

15. Sodium Bicarbonate, $NaHCO_3$.—Prepare a *strong* solution of caustic soda by dissolving 5 grams of stick soda in 10 c.c. of distilled water. When the liquid is cold (cool it under the tap) pass a current of carbon dioxide through it. The gas is prepared by the action of dilute hydrochloric acid on lumps of limestone or marble contained in a flask (or a Kipp's apparatus may be used) and washed free from hydrochloric acid by passing through water in a flask or wash-bottle.

After the gas has been passing through the caustic soda for some time a white powder separates out. When no more precipitate appears to form, filter and wash with a very little cold water. Now dry the powder between filter paper and examine it with a lens: note that it is crystalline.

The formation of the salt takes place in two stages. The normal carbonate is first formed, since caustic soda is in excess, according to the equation

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

This remains in solution, but as more carbon dioxide is passed the bicarbonate is formed, and being much less soluble crystallises out—

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3.$$

The bicarbonate may also be readily prepared by making a saturated solution of washing soda and passing carbon dioxide through it. Crystals separate out as before.

16. Sodium Carbonate, Washing Soda, $Na_2CO_3.10H_2O$.—Pass carbon dioxide, prepared as in the previous experiment, through a *boiling* dilute solution of caustic soda till the gas ceases to be absorbed. Now allow the liquid to cool: large transparent crystals separate out, having the composition $Na_2CO_3.10H_2O$. These should be filtered off, washed with a little water, and dried between filter paper.

17. Caustic Potash, KOH, from Potassium Carbonate, K_2CO_3.—Weigh out 10 grams of potassium carbonate and dissolve in 150 c.c. of distilled water in a porcelain dish. Now add 5 grams of slaked lime, *i.e.* rather more* than the quantity required to decompose the potassium carbonate according to the equation

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3.$$

* The slaked lime will most probably be less pure than the potassium carbonate.

Heat the mixture to the boiling point with stirring and continue to boil till a filtered sample of the supernatant liquid after settling no longer effervesces on the addition of dilute hydrochloric acid.* Now filter off the precipitate of calcium carbonate, evaporate the filtrate till a sample solidifies on cooling, and then allow the whole to solidify.

Test the freedom of the preparation from (1) potassium carbonate, (2) calcium hydroxide.

(1) *Potassium Carbonate.*—Break off a piece of the potash, dissolve it in distilled water and add a little dilute hydrochloric acid; there should be no effervescence.

(2) *Calcium Hydroxide.*—Dissolve another piece of the potash in water and add some ammonium or sodium carbonate solution. There should only be a slight precipitate of calcium carbonate, showing that only a trace of calcium hydroxide is present.

$$Ca(OH)_2 + (NH_4)_2CO_3 = \underset{\downarrow}{CaCO_3} + 2NH_4OH.$$

$$Ca(OH)_2 + Na_2CO_3 = \underset{\downarrow}{CaCO_3} + 2NaOH.$$

18. Potassium Iodide, KI.—Dissolve 7 grams of caustic potash in the minimum quantity of water, and add iodine gradually till the liquid acquires a permanent yellow colour, showing that the potash has dissolved as much iodine as it can take up (about 16 grams will be required).

The solution now contains a mixture of potassium iodide and iodate formed according to the equation

$$6KOH + 3I_2 = 5KI + KIO_3 + 3H_2O.$$

Evaporate the liquid to dryness, powder the residue in a mortar, and mix it *thoroughly* with about 5 grams of powdered charcoal. Introduce the mixture into a porcelain crucible and cover with the lid. Now support the crucible on a pipe-clay triangle and heat to redness by means of a Bunsen burner, maintaining at this temperature for about

* It may be necessary to add a little more slaked lime in order to bring this about, owing to the impurities in the lime.

half an hour. The potassium iodate will by this time be completely reduced to iodide according to the equation

$$KIO_3 + 3C = KI + 3CO.$$

Extract the product with hot distilled water, filter, and evaporate in a dish on the water-bath till a drop of the liquid removed on the end of a glass rod crystallises. Now allow the liquid to crystallise, filter off the crystals, wash with a little cold water, and dry between folds of filter paper.

Test the freedom of the specimen from iodate by dissolving a little in water, acidifying with dilute sulphuric acid, and then adding freshly prepared starch solution. If any iodate is present, the characteristic blue colour of iodide of starch will develop. This is explained by the fact that iodic and hydriodic acids (set free in this case by the addition of sulphuric acid to their potassium salts) at once mutually decompose each other with separation of iodine according to the equation

$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

The liberated iodine is identified by the starch test.

19. Potassium Chlorate, $KClO_3$.—Weigh out 50 grams of slaked lime, mix it with 150 c.c. of hot distilled water and pass chlorine through the mixture to saturation (*i.e.* till the liquid smells strongly of the gas).

Prepare the chlorine by introducing 20 grams of manganese dioxide in small lumps into a $\frac{3}{4}$ litre flask, just covering it with concentrated hydrochloric acid and warming gently; wash the gas by passing through a little water in a flask.

The formation of chlorine is thus represented—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2;$$

its action on hot milk of lime thus—

$$6Ca(OH)_2 + 6Cl_2 = \underset{\text{Calcium chlorate}}{Ca(ClO_3)_2} + 5CaCl_2 + 6H_2O.$$

The liquid, therefore, now contains calcium chlorate and chloride in solution. Filter and evaporate down to about

half the bulk. Now add 12 grams of potassium chloride dissolved in the minimum quantity of water, *i.e.* a quantity of the salt in slight excess of that required to bring about a double decomposition with the calcium chlorate according to the equation

$$Ca(ClO_3)_2 + 2KCl = 2KClO_3 + CaCl_2.$$

Evaporate down the solution to about half its bulk and leave to stand. Potassium chlorate, being much the least soluble salt present, crystallises out. Filter off the crystals, wash them with a little water and recrystallise by dissolving in the minimum quantity of hot distilled water and leaving to cool. Finally filter off the crystals which separate, wash them with a little distilled water and dry them between filter paper.

Test the purity of the preparation by dissolving some of the crystals in distilled water and adding silver nitrate solution. If chloride is present as impurity a white precipitate of silver chloride will be formed; otherwise there will be no precipitate, as silver chlorate is a soluble salt.

20. Potassium Permanganate, $KMnO_4$.—Weigh out 10 grams of manganese dioxide and 9 grams of potassium chlorate, and grind them together in a mortar till they are thoroughly mixed. Now weigh out 13 grams of caustic potash and dissolve in the minimum quantity of water. Transfer the mixture of manganese dioxide and potassium chlorate to an iron* dish and pour the potash solution over it. Evaporate the mixture to dryness on a sand bath and then heat strongly over a Bunsen flame for about a quarter of an hour. This results in the formation of potassium manganate, K_2MnO_4, the reaction which takes place being represented by the equation

$$3MnO_2 + KClO_3 + 6KOH = \underset{\text{Potassium manganate}}{3K_2MnO_4} + KCl + 3H_2O.$$

* A porcelain dish must be used if an iron one is not available, but the latter is preferable, as it is much less readily attacked by caustic potash.

It is necessary, however, to use excess of potassium chlorate, and nearly twice the theoretical quantity required by the equation was employed.

Now allow the dish to cool, powder the residue in a mortar and shake it up with water in a flask. The potassium manganate dissolves with formation of a dark green solution.

Next pass a current of carbon dioxide into the liquid for about half an hour. This converts three-quarters of the potassium manganate into the permanganate, the remainder forming a brown precipitate of hydrated manganese sesquioxide according to the equation

$$8K_2MnO_4 + 5CO_2 + H_2O = 6KMnO_4 + 5K_2CO_3 + Mn_2O_3 . H_2O.$$

Introduce a pad of glass wool or asbestos fibre into a filter funnel and filter the mixture through this (as potassium permanganate attacks filter paper). Evaporate the filtrate to small bulk and leave to crystallise. Decant off the liquid, wash the crystals with a little distilled water and leave them on a clock glass in a warm place to dry.

The oxidising action of the crystals should be demonstrated by dissolving some of them in water, when a deep purple solution will be formed, and treating small portions with (1) sulphurous acid, (2) dilute sulphuric acid followed by ferrous sulphate solution, (3) dilute sulphuric acid followed by hot oxalic acid solution. In each case the purple colour will disappear.

The reactions taking place are represented by the following equations:—

$$2KMnO_4 + 5H_2SO_3 = 2KHSO_4 + 2MnSO_4 + H_2SO_4 + 3H_2O$$

$$2KMnO_4 + 10FeSO_4 + 9H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

$$2KMnO_4 + 5C_2H_2O_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

21. Hydrated Calcium Chloride, $CaCl_2.6H_2O$.—Take about 20 c.c. of dilute hydrochloric acid in an evaporating

basin; add chalk or marble until some remains undissolved. Filter, and evaporate the filtrate till a drop of the liquid removed on the end of a glass rod crystallises. Allow to cool. Pour off the liquid from the crystals which separate and dry these between filter paper as quickly as possible.

The colourless crystals you have prepared have the composition $CaCl_2.6H_2O$. Leave some of them exposed to the air and note that they rapidly deliquesce. Heat another portion in a test-tube. Note that the crystals melt and then lose water, which condenses in the cool part of the tube, and that a white residue remains behind. This residue is anhydrous calcium chloride, $CaCl_2$. Leave it exposed to the air and note that it also rapidly deliquesces.

22. Hydrated Calcium Nitrate, $Ca(NO_3)_2.4H_2O$.—This salt is prepared by a method similar to that used for calcium chloride in the previous preparation, using dilute nitric acid in place of dilute hydrochloric acid.

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2.$$

The colourless crystalline salt which is obtained has the formula $Ca(NO_3)_2 . 4H_2O$, and, like the corresponding chloride, is very deliquescent.

23. Hydrated Ferrous Chloride, $FeCl_2 . 4H_2O$.—Fit a half-litre flask with a cork through which passes a short piece of glass tubing. Introduce 10 grams of pure iron wire into the flask, add 40 c.c. of concentrated hydrochloric, and push in the cork. Hydrogen is evolved with effervescence and ferrous chloride goes into solution.

$$Fe + 2HCl = FeCl_2 + H_2.$$

The almost complete closing of the flask by the cork and tube prevents the oxidation of the ferrous chloride, for the hydrogen evolved in the reaction soon drives the air out of the flask.

When all the iron has dissolved (add a little more acid if necessary) leave the solution to crystallise. Bluish

crystals having the composition $FeCl_2,4H_2O$ separate out. Pour off the supernatant liquid and wash the crystals with a *little* cold distilled water. Then shake them out, dry them quickly between filter paper, and bottle them at once.

The success of this preparation depends on excluding air as completely as possible, owing to the readiness with which ferrous chloride takes up oxygen. This should be demonstrated by leaving a few of the crystals exposed to the air for a short time, when they will be observed to deliquesce and become greenish.

24. Anhydrous Ferrous Chloride, $FeCl_2$.—N.B. This preparation should be carried out in a fume cupboard.

Procure a rather wide hard glass tube about 40 cm. long and provided with a bulb near one end. Introduce into the other end of the tube a closely wound spiral of

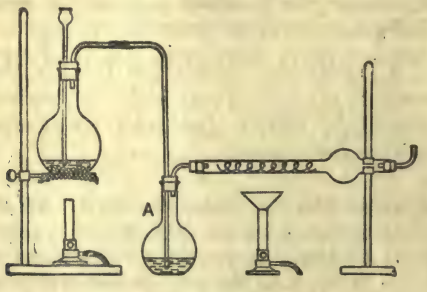

Fig. 6.

iron wire. Fit the bulb end of the tube with a cork through which passes a short piece of glass tubing. Support the tube by a retort stand and clamp, as shown in Fig. 6.

Now connect the tube with an apparatus for preparing *dry* hydrogen chloride. This consists of a generator similar to that used in Preparation 2, and a small flask (or bottle), A, containing concentrated sulphuric acid,

which serves to dry the gas.* Start the current of gas, and when it begins to fume at the exit tube (showing that the air has been expelled from the apparatus) heat the iron spiral by means of a spreading Bunsen flame. After a time white feathery crystals, consisting of ferrous chloride, will begin to collect in the bulb.

When the iron wire is used up the crystals may be shaken out of the bulb and bottled.

Leave a few of the crystals exposed to the air and note that they rapidly deliquesce.

25. Ferric Chloride Solution, $FeCl_3$.Aq.—Prepare a solution of ferrous chloride in a flask by dissolving 5 gm. of iron wire or filings† in hydrochloric acid. Pass chlorine through part of the solution till the liquid smells strongly of the gas (keeping the other part corked up in the flask to exclude air); notice that the almost colourless solution has become brown. Now heat till the smell of chlorine has disappeared.‡

The solution now contains ferric chloride, produced by the direct combination of ferrous chloride and chlorine.

$$2FeCl_2 + Cl_2 = 2FeCl_3.$$

In order to prove this, compare the action of (1) caustic soda, (2) hydrochloric acid and potassium permanganate on (*a*) the brown solution, (*b*) the remainder of the ferrous chloride solution (through which chlorine has not passed).

You will see that ferrous chloride gives a *greenish* precipitate with caustic soda and *decolorises* potassium permanganate, but after passing chlorine through the solution to saturation, caustic soda gives a *brown* precipitate and the solution *does not decolorise* potassium permanganate.

* It is preferable to use *two* drying flasks.

† If *filings* are used the solution must be filtered from carbon particles before chlorine is passed through it.

‡ If any precipitate forms it should be redissolved by adding hydrochloric acid

Ferrous chloride gives a precipitate of ferrous hydroxide with caustic soda, whereas ferric chloride gives a brown precipitate of ferric hydroxide.

$$FeCl_2 + 2NaOH = Fe(OH)_2 + 2NaCl.$$
$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl.$$

Also ferrous chloride is a reducing agent and decolorises potassium permanganate, the reaction being represented thus—

$$10FeCl_2 + 16HCl + 2KMnO_4 = 10FeCl_3 + 2KCl + 2MnCl_2 + 8H_2O.$$

Ferric chloride, on the other hand, does not possess reducing properties.

6. Anhydrous Ferric Chloride, $FeCl_3$.—Prepare this salt by passing dry chlorine over heated iron wire, using an apparatus similar to that employed in preparing anhydrous ferrous chloride (Preparation 24) and working in a fume cupboard. Nearly black shining crystals of the salt collect in the bulb.

$$2Fe + 3Cl_2 = 2FeCl_3.$$

Prepare the chlorine as described under Preparation 19 and dry it by passing through two sulphuric acid wash bottles. Show that the crystals you obtain are very deliquescent by exposing some of them to the air for a short time.

27. Ferric Oxide, Fe_2O_3.—*Method 1. From ferric chloride.*—Introduce about 20 c.c. of ferric chloride solution into a beaker, raise to the boiling point, and add a boiling solution of ammonia gradually with stirring. When the precipitation of brown ferric hydroxide appears to be complete, allow the liquid to settle, and then add a drop more ammonia solution. If a further precipitate is formed add more ammonia, stir up the liquid, allow to settle, and again test whether precipitation is complete by adding another drop of ammonia. Add more ammonia if

necessary, and when the test shows that the reaction is complete, filter and wash the precipitate several times with hot distilled water.

Now dry the precipitate on the water bath (or in a steam oven) and transfer it to a porcelain crucible. Support the crucible by means of a pipe-clay triangle and heat it over a Bunsen burner for about 20 minutes. The grey solid which remains is ferric oxide, produced from the ferric hydroxide by loss of water.

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$$

When the crucible is cold turn the contents out into a mortar and grind them up. The colour of the powder will be *red.* (Ferric oxide varies in colour according to the precise mode of preparation, but all forms when powde red acquire some shade of red.)

Method 2. From metallic iron.—Weigh out 5 grams of iron filings in a porcelain dish, cover with concentrated nitric acid and leave in a fume chamber. The filings dissolve with evolution of reddish-brown fumes (nitrogen peroxide) and formation of a brown solution of ferric nitrate, $Fe(NO_3)_3$.

$$Fe + 6HNO_3 = Fe(NO_3)_3 + 3NO_2 + 3H_2O.$$

Evaporate the solution to dryness on the water bath, and then heat on a sand bath till reddish-brown fumes cease to be evolved. Ferric oxide remains as a grey crystalline powder.

$$4Fe(NO_3)_3 = 2Fe_2O_3 + 12NO_2 + 3O_2.$$

28. Magnetic Oxide of Iron, Fe_3O_4.—Weigh out 2 grams of ferrous sulphate crystals, dissolve in water, acidify with sulphuric acid, add some nitric acid, and boil till brown fumes cease to be evolved even on the addition of a few more drops of nitric acid. Now add caustic potash to the solution till a precipitate begins to form * and *just* redissolve this with dilute sulphuric acid.

* The object of this is to neutralise the excess of nitric acid so that it does not oxidise the ferrous sulphate subsequently added.

Next weigh out 1 gram of ferrous sulphate crystals, dissolve in water, and add the solution to that just prepared. Shake up in order to mix thoroughly and then add caustic potash. Filter off the black precipitate which forms, wash it, and dry on the water bath.

Powder the brownish-black solid which is obtained and test it with a magnet: it is attracted.

The magnetic solid which you have prepared is *magnetic oxide of iron*, Fe_3O_4 (combined with a little water). The changes which have taken place are as follows:—The ferrous sulphate which you boiled with nitric acid was oxidised to ferric sulphate, according to the equation

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

The ferric sulphate formed was equivalent to *two* grams of ferrous sulphate, and you subsequently added *one* gram of ferrous sulphate, so that the solution to which you added caustic potash contained equal numbers of molecules of ferrous and ferric sulphates (since each molecule of ferric sulphate is formed from two molecules of ferrous sulphate—see equation above).

The effect of adding caustic potash to this solution is to produce a black precipitate, which may be considered as a compound of equal numbers of molecules of ferrous and ferric hydroxides, and this compound when dried on the water bath loses water, and is converted into magnetic oxide of iron, which we may consider as a compound of one molecule of ferrous oxide and one molecule of ferric oxide.

One molecule of ferrous oxide	$= FeO$
„ „ „ ferric oxide	$= Fe_2O_3$
„ „ „ magnetic oxide of iron	$= Fe_3O_4$

29. Iron Ammonium Alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$.—Dissolve 10 gm. of ferrous sulphate crystals in distilled water, add 10 c.c. of dilute sulphuric acid, and oxidise to ferric sulphate by means of nitric acid as in

the last preparation. When the oxidation is complete evaporate nearly to dryness, to drive off excess of nitric acid, and then add sufficient hot water to redissolve any salt which has separated out.

While the evaporation is proceeding weigh out 4·8 gm. of ammonium sulphate (*i.e.* a quantity equivalent to the ferric sulphate produced in the preceding process) and dissolve it in the minimum quantity of hot water.

Now mix the two solutions and leave to crystallise. The crystals which separate consist of iron ammonium alum and are formed by the combination of the two sulphates in solution. Filter them off, wash with a little cold distilled water, and dry between filter paper.

30. Cupric Oxide, CuO.—Introduce about 5 grams of copper turnings into a porcelain dish, cover them with nitric acid diluted with its own volume of water, and leave in a fume chamber. The metal will dissolve with effervescence and formation of reddish-brown fumes (nitrogen peroxide). When solution is complete, evaporate the liquid (which is a solution of copper nitrate, $Cu(NO_3)_2$) to dryness on the water bath. Blue crystals of the composition $Cu(NO_3)_2.3H_2O$ remain behind. Now heat the basin carefully on a sand bath. The crystals melt and then decompose, giving off reddish-brown fumes (nitrogen peroxide). Continue the heating till the evolution of reddish-brown fumes ceases and the residue, which changes to green at first, has become black. The residue now consists of cupric oxide, formed by decomposition of the cupric nitrate according to the equation

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

31. Cuprous Oxide, Cu_2O.—Weigh out 5 grams of copper sulphate crystals and dissolve in distilled water. Also prepare an aqueous solution containing 2·5 grams of Rochelle salt (sodium potassium tartrate) and 1·5 grams of caustic soda. Now mix the two solutions in a beaker. The Rochelle salt prevents the precipitation of the copper by the alkali. Finally weigh out a gram of grape sugar

(dextrose), dissolve in distilled water, and add to the alkaline copper solution. Warm gently. A red (momentarily yellow) precipitate of cuprous oxide rapidly forms as a result of the reducing action of the grape sugar. When on allowing the liquid to settle the blue colour is seen to have disappeared, the reduction of the copper is complete.

Now filter off the precipitate, wash with distilled water till free from alkali, and dry on the water bath or in the steam oven.

Add ammonia to a little of the dry powder. Note that it dissolves, forming a colourless solution which rapidly becomes blue owing to absorption of oxygen from the air.

32. Hydrated Copper Sulphate, $CuSO_4.5H_2O$.—*Method 1. From cupric oxide.*—Add finely powdered cupric oxide gradually to 50 c.c. of hot dilute sulphuric acid contained in a flask, shaking up after each addition. The oxide dissolves, forming a blue solution of copper sulphate.

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

When no more oxide dissolves filter the liquid, evaporate down somewhat on the water bath and allow to stand. Blue crystals having the composition $CuSO_4.5H_2O$ separate out. Pour off the supernatant liquid, wash the crystals by decantation with a little distilled water and dry between filter paper.

Method 2. From metallic copper.—Introduce about 5 grams of copper turnings into a flask and cover with concentrated sulphuric acid. Heat gently on a sand bath in a fume cupboard. Sulphur dioxide is evolved with effervescence, and after a time a dark greyish powder settles at the bottom of the flask. This consists of a mixture of monohydrated copper sulphate, $CuSO_4.H_2O$ (bluish-white), and cuprous sulphide, Cu_2S (black), both of these compounds being insoluble in concentrated sulphuric acid. The main reaction taking place may be represented by the equation

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

The formation of cuprous sulphide is due to a secondary reaction.

$$5Cu + 4H_2SO_4 = 3CuSO_4 + Cu_2S + 4H_2O.$$

When the copper has disappeared allow the mixture to cool and then carefully pour off the liquid from the grey residue. Now add some distilled water to this and shake up. The monohydrated copper sulphate dissolves forming a blue solution, whilst the cuprous sulphide remains as an insoluble black powder. Filter this off, evaporate the filtrate to small bulk, and allow to crystallise. Separate, wash, and dry the crystals as in Method 1.

33. Hydrated Cupric Chloride, $CuCl_2.2H_2O$.—Introduce 50 c.c. of dilute hydrochloric acid into a flask, heat, and then add finely powdered cupric oxide little by little, shaking after each addition. The oxide dissolves forming a solution of cupric chloride, which is greenish or bluish according to the state of dilution.

$$CuO + 2HCl = CuCl_2 + H_2O.$$

When the oxide ceases to dissolve filter the solution, evaporate down somewhat on the water bath, and leave to crystallise. Greenish-blue crystals separate out, having the composition represented by the formula $CuCl_2.2H_2O$. Pour off the mother liquor, wash the crystals with a little cold distilled water, and dry between filter paper.

Dissolve a little of the salt in water and add ammonia solution. A deep blue liquid is formed, due to the combination of the cupric chloride with ammonia to form the compound $CuCl_2.4NH_3$.

34. Cuprous Chloride, Cu_2Cl_2.—Make a strong solution of copper sulphate by dissolving 5 grams of the crystals in about 15 c.c. of water in a flask of about 200 c.c. capacity. Add to the solution 2·5 grams of common salt, 40 c.c. of concentrated hydrochloric acid, and finally 5 grams of copper turnings. Boil the solution for about half an hour in the fume cupboard. Cuprous chloride is formed and goes into solution in the strong hydrochloric acid.

We may suppose that the copper sulphate and common salt first undergo double decomposition with formation of cupric chloride and sodium sulphate according to the equation $CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4$.

The cupric chloride then unites with copper in the presence of hydrochloric acid to form cuprous chloride.

$$CuCl_2 + Cu = Cu_2Cl_2.$$

Pour off the liquid from the undissolved copper into several times its volume of water, when a white precipitate is thrown down. This is the cuprous chloride which is almost insoluble in sufficiently diluted hydrochloric acid. Filter and wash the precipitate with distilled water several times. Collect a few drops of the liquid running through the filter on a watch-glass from time to time and evaporate to dryness by holding some distance above a Bunsen flame. When practically no solid residue remains on the watch-glass the cuprous chloride has been washed free from solid impurities. Now press the precipitate between filter paper and dry it finally in a steam oven or on the water bath.

Shake up a little of the product with some ammonia solution. It dissolves, giving a colourless solution (if pure), but the liquid rapidly becomes blue owing to absorption of oxygen.

35. Basic Copper Carbonate.—Add sodium carbonate solution gradually with stirring to about 20 c.c. of a solution of copper sulphate till a small quantity of the filtered liquid gives no precipitate on the addition of sodium carbonate.

Filter off the blue precipitate, which is basic copper carbonate, *i.e.* a compound of the normal carbonate, $CuCO_3$, and the hydroxide, $Cu(OH)_2$ (in varying proportions which depend on the precise conditions of the experiment—temperature, etc.).

Wash the precipitate as free from alkali as possible with distilled water, and dry in the steam oven or on the water bath.

36. Lead Dioxide, Puce Oxide of Lead, PbO_2.—Warm about 25 c.c. of dilute nitric acid in a porcelain dish and then add 5 grams of red lead, Pb_3O_4, and stir. Note that the *red* colour of the powder changes to *brown*. When this change is complete, filter and wash the residue with hot distilled water till a drop of the liquid running through the filter leaves no residue on evaporation to dryness (showing that all the lead nitrate formed in the reaction has been removed); finally dry it on the water bath or in a steam oven.

The brown residue is lead dioxide formed according to the reaction expressed by the following equation:—

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

Heat a little of the oxide with concentrated hydrochloric acid and show that it dissolves with evolution of chlorine (identified by its colour, smell, and action on litmus paper).

$$PbO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O.$$

The lead chloride formed in the reaction separates out as white crystals as the solution cools.

Now heat a little of the oxide with concentrated sulphuric acid and show that oxygen is evolved (glowing match test). Note that the brown oxide is converted into a white insoluble powder, lead sulphate.

$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2.$$

37. Lead Chloride, $PbCl_2$.—Dissolve about 5 grams of lead in dilute nitric acid in a beaker (in the fume cupboard). The solution contains lead nitrate. Now add dilute hydrochloric acid: a white precipitate of lead chloride is formed.

$$Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3.$$

Allow the precipitate to settle and then add more hydrochloric acid in order to test whether the precipitation is complete. When this is the case, filter off the precipitate and wash it with a little distilled water. Now transfer it to a beaker and add boiling water gradually with stirring

till the precipitate dissolves. Leave to crystallise. The salt separates out in beautiful shining crystals, being much less soluble in cold water than in hot. Filter these off, wash them with a little cold water, and dry between filter paper and then on the water bath or in a steam oven.

38. "White Lead," Basic Lead Carbonate, $(PbCO_3)_2.Pb(OH)_2$.—Add 5 grams of litharge (PbO) to 25 c.c. of lead acetate solution contained in a flask and boil for 10 minutes. Filter from undissolved litharge. The solution now contains basic lead acetate, $Pb(C_2H_3O_2)_2.Pb(OH)_2$.

$$\underset{\text{Lead acetate}}{Pb(C_2H_3O_2)_2} + PbO + H_2O = \underset{\text{Basic lead acetate}}{Pb(C_2H_3O_2)_2, Pb(OH)_2}.$$

Now pass a current of carbon dioxide through this solution. A white precipitate of "white lead" is formed according to the reaction expressed by the equation

$$3[\underset{\text{Basic lead acetate}}{Pb(C_2H_3O_2)_2.Pb(OH)_2}] + 2CO_2 = \underset{\text{White lead}}{(PbCO_3)_2, Pb(OH)_2} + 3\underset{\text{Lead acetate}}{Pb(C_2H_3O_2)_2} + 2H_2O.$$

When the precipitation appears to be complete stop the current of carbon dioxide and allow the precipitate to settle. Now pass a little more carbon dioxide through the supernatant liquid to test whether the precipitation is complete. If it is not, continue the passage of gas for a short time, allow to settle, and test again as before. When the precipitation is complete, filter, wash the precipitate with cold distilled water till a drop of the filtrate gives only a faint opalescence with dilute sulphuric acid (due to the precipitation of lead sulphate from the lead acetate in solution), and dry it on the water bath or in the steam oven.

CHAPTER II.

ACTION OF HEAT ON SOME TYPICAL SUBSTANCES.

The following experiments, in which the action of heat on some single substances and mixtures of substances is investigated, will serve to train the student's powers of observation. Accurate notes should be taken at the time of each experiment, all that is observed being carefully recorded. Similar investigations may be carried out with other substances as time and opportunity permit.

Exp. 1. Action of Heat on Lead Dioxide, PbO_2.—Introduce a small quantity of lead dioxide (puce oxide of lead) into a hard glass tube closed at one end. Have by you a splinter of wood long enough to reach to the bottom of the tube. Now heat the tube in the hottest part of the flame (*i.e.* near the tip). Ignite the splinter, blow out the flame, and thrust the glowing end down the tube. You will observe that the glowing splinter bursts into flame, showing that oxygen is being evolved. Allow the tube to cool. The solid residue becomes yellow and consists of litharge, PbO. The decomposition is represented by the equation

$$\underset{\text{Lead dioxide}}{2PbO_2} = \underset{\text{Litharge}}{2PbO} + O_2.$$

N.B.—Litharge is *yellow* when *cold*, but darkens in colour on heating, and if the temperature is sufficiently high it melts to a dark red liquid.

Exp. 2. Action of Heat on Potassium Bicarbonate, $KHCO_3$.—Introduce some potassium bicarbonate into a test-tube fitted with a cork and bent delivery tube, which

dips into a solution of lime water. Heat the test-tube in a Bunsen flame. In a short time you will observe that a gas is evolved which renders the lime water milky (at first air is, of course, driven out of the tube). This gas is carbon dioxide, produced by the decomposition of the potassium bicarbonate according to the equation

$$\underset{\text{Potassium bicarbonate}}{2KHCO_3} = \underset{\text{Potassium carbonate}}{K_2CO_3} + H_2O + CO_2$$

When evolution of gas ceases, remove the cork and delivery tube, and then discontinue heating the test-tube. The white residue which remains behind is normal potassium carbonate, K_2CO_3, the decomposition being precisely similar to that which takes place when sodium bicarbonate (baking soda) is heated as expressed by the equation

$$\underset{\text{Sodium bicarbonate}}{2NaHCO_3} = \underset{\text{Sodium carbonate}}{Na_2CO_3} + H_2O + CO_2.$$

When the test-tube is cold dissolve the residue of potassium carbonate in water and test it with red litmus paper: note that it is *strongly* alkaline (like sodium carbonate). Also test a solution of potassium bicarbonate with red litmus paper and note that it is only *slightly* alkaline (like sodium bicarbonate).

Now prove that the solution of potassium carbonate does actually contain a carbonate by adding some dilute hydrochloric acid, noting the effervescence and passing the gas evolved into lime water, which becomes milky (or you may introduce a drop of lime water into the tube on the end of a glass rod).

Exp. 3. Action of Heat on Potassium Chlorate, $KClO_3$.—Heat gently a small quantity of potassium chlorate in a test-tube by means of a Bunsen flame. Notice that the salt first crackles,* then melts, and at last seems to boil—

* The crackling is due to drops of water which are enclosed in the crystals. These expand into steam and so break the crystals open. If the crystals are quite small there is no crackling.

owing to the evolution of gas. Show that this gas is oxygen by testing with a glowing splinter. As the heating is continued you will notice that after a time the liquid thickens and that the evolution of gas slackens. Now heat somewhat more strongly. The evolution of gas again becomes rapid for a time and the residue becomes more liquid. Finally the evolution of gas ceases and a white solid residue remains behind. If, however, the heating is sufficiently strong this residue melts to a colourless liquid.

During the first stage of the reaction two changes take place simultaneously, namely the decomposition of potassium chlorate into potassium chloride and oxygen according to the equation

$$2KClO_3 = 2KCl + 3O_2,$$

and the decomposition of the chlorate into potassium perchlorate and chloride as expressed by the equation

$$4KClO_3 = \underset{\text{Potassium perchlorate}}{3KClO_4} + KCl.$$

It is the formation of the perchlorate which produces the thickening you noticed at the close of the first stage of the decomposition.

When the heating was continued more strongly the potassium perchlorate decomposed into potassium chloride and oxygen as represented by the equation

$$KClO_4 = KCl + 2O_2.$$

The potassium chloride remained as a white solid, which only melts on strongly heating.

When the tube has cooled down, dissolve the residue in water, and prove the presence of potassium chloride in the solution by adding a little silver nitrate solution, when a white precipitate of silver chloride is formed.

$$KCl + AgNO_3 = AgCl + KNO_3.$$

Potassium chlorate and perchlorate give no precipitate with silver nitrate, as the corresponding silver salts are soluble.

Exp. 4. Action of Heat on Potassium Nitrate, KNO_3.—Heat a little nitre in a test-tube. It crackles and flies about, then fuses, and at higher temperature a gas is evolved. Show by means of the glowing splint test that this gas is oxygen. When the evolution of gas ceases allow the tube to cool; the residue solidifies to a white mass.

Now add some water and shake up: you will find that the white residue dissolves. Next add a little dilute sulphuric or hydrochloric acid to the residue, and note that it dissolves with effervescence and formation of reddish-brown fumes having the characteristic odour of nitrogen peroxide. The white residue was potassium nitrite, which gives nitrous acid on acidification; the nitrous acid at once decomposes with formation of reddish-brown fumes.

The decomposition of potassium nitrate on heating is represented by the equation

$$\underset{\text{Potassium nitrate}}{2KNO_3} = \underset{\text{Potassium nitrite}}{2KNO_2} + O_2.$$

Exp. 5. Action of Heat on Crystallised Calcium Nitrate $Ca(NO_3)_2.4H_2O$.—Prepare some crystals of hydrated calcium nitrate as described in Preparation 22. Introduce them into a test-tube and heat. The crystals melt and lose water, which condenses in the upper part of the tube, and the anhydrous salt remains as a white porous mass. Now heat this further. It decomposes, giving off reddish-brown fumes of nitrogen peroxide, and a white powdery residue remains behind. Allow the tube to cool, and add water to the white residue drop by drop. Note that the residue becomes hot. Now add water in quantity, when you will find that the residue dissolves. Test the solution with red litmus paper: it is alkaline.

The white residue is quicklime, CaO, and the decomposition of calcium nitrate under the action of heat is expressed by the equation

$$2Ca(NO_3)_2 = 2CaO + 4NO_2 + O_2.$$

Exp. 6. Action of Heat on Ammonium Nitrate, NH_4NO_3.—Heat some crystals of ammonium nitrate *gently* in a test-tube. They melt and then give off a gas which you will find rekindles a glowing splint just as oxygen does. Now introduce a little *feebly* burning sulphur into the tube on the end of a bit of wire. The flame is extinguished, showing that the gas is not oxygen. It is *nitrous oxide*.

Next heat the tube *strongly*. The decomposition is now accompanied by explosions, and when it is complete no solid remains in the tube.

The decomposition is represented by the equation

$$NH_4NO_3 = N_2O + 2H_2O.$$

Exp. 7. Action of Heat on Ammonium Dichromate $(NH_4)_2Cr_2O_7$.—Fit a test-tube with a cork and bent delivery tube. Place in the tube a few crystals of the reddish compound ammonium dichromate, fit in the cork and delivery tube, and heat gently. Suddenly a brisk agitation will be set up, the larger red crystals rapidly disintegrating into finer green particles with increase of volume. A gas is also evolved which is colourless. Bubble a little through lime water; no milkiness is produced. Remove the cork and test the gas with a lighted match. The gas does not burn, nor does it support combustion. It has neither taste nor smell. It is nitrogen.

The green powder which remains behind is chromium sesquioxide, Cr_2O_3. Test its solubility, and also that of ammonium dichromate in water: you will find that the latter is soluble, the former not.

The decomposition of ammonium dichromate by heat is expressed by the equation

$$\underset{\text{Ammonium dichromate}}{(NH_4)_2Cr_2O_7} = N_2 + 4H_2O + \underset{\text{Chromium sesquioxide}}{Cr_2O_3}.$$

Exp. 8. Action of Heat on Crystallised Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$.—Introduce a few crystals of sodium thiosulphate into a test-tube and heat gently in a Bunsen flame. The salt melts, and the liquid soon boils and gives off steam, part of which condenses in the cool part of the

tube. After a time a white solid begins to separate out, and soon the whole mass becomes changed into this white solid. The water driven off is derived from the water of crystallisation of the salt, and the white residue is anhydrous sodium thiosulphate.

Now continue the heating. The residue darkens, soon becoming almost black; at the same time it melts (at any rate in part). A yellow powder collects on the sides of the tube, and below this, where the tube is hot, a yellow liquid; also the characteristic odour of sulphuretted hydrogen is noticeable. The yellow powder is "flowers of sulphur" (and the yellow liquid melted sulphur), as may be shown by scraping some out after the tube has been allowed to cool and heating it in a Bunsen flame on a bit of broken pot; it burns with a blue flame and the characteristic odour of "burning sulphur."

When the tube has cooled it will be found that an orange-coloured solid remains. Add some distilled water to this and boil. A considerable part of the residue dissolves, forming a brown solution. Filter and add to the filtrate a little hydrochloric acid. You will note that a white precipitate of sulphur (changing to yellow) is formed and sulphuretted hydrogen evolved.

The changes which take place during the second stage of the heating of sodium thiosulphate are of a complex nature, and the residue contains a number of sodium salts, including polysulphides and the sulphate, together with free sulphur. The presence of the polysulphides explains the action of hydrochloric acid on the brown solution obtained above; that of free sulphur accounts for the dark colour of the residue both when cold and also when hot (since liquid sulphur at high temperature is nearly black).

Exp. 9. Action of Heat on Microcosmic Salt, $Na(NH_4)HPO_4$, $4H_2O$.—Heat gently a small quantity of microcosmic salt in a test-tube. The salt melts readily and gives off water which condenses in the cool part of the tube. Ammonia is also evolved and may be detected by its odour and action on moist red litmus paper. When the decom-

position is complete a solid residue remains which consists of sodium dihydrogen orthophosphate, NaH_2PO_4. The change which has taken place is represented by the equation

$$Na(NH_4)HPO_4.4H_2O = NaH_2PO_4 + NH_3 + 4H_2O.$$

Now heat the residue in the hottest part of the flame (near the tip). The solid residue melts and water is again given off. The clear liquid which is formed solidifies on cooling to a glassy mass consisting of sodium metaphosphate, $NaPO_3$. This stage of the decomposition is represented by the equation

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

Dissolve the cold residue in water and add to it a solution of silver nitrate: a *white* precipitate of silver metaphosphate, $AgPO_3$, is formed.

$$NaPO_3 + AgNO_3 = \underset{\text{White precipitate}}{AgPO_3} + NaNO_3$$

Now dissolve some microcosmic salt in water and add silver nitrate solution: a *yellow* precipitate of silver phosphate, Ag_3PO_4, is formed.

$$Na(NH_4)HPO_4 + 3AgNO_3 = \underset{\text{Yellow precipitate}}{Ag_3PO_4} + NaNO_3 + HNO_3 + NH_4NO_3.$$

Exp. 10. Action of Heat on Green Vitriol, Crystallised Ferrous Sulphate, $FeSO_4.7H_2O$.—Heat some clean crystals of green vitriol in a test-tube, holding the tube with the open end directed downwards, so that any liquid formed does not run back into the hot part of the tube. Have a second tube held under the mouth of the first to catch any of the condensed liquid which runs out.

The first effect of the heating is that the crystals melt and give off steam which condenses in the cool part of the tube as a colourless liquid; a dirty white solid remains behind. As the heating is continued acid fumes come off and these dissolve in the condensed water; at the same time

the colour of the residue becomes yellow and then reddish-brown. This reddish-brown solid represents the final stage in the decomposition and consists of ferric oxide, Fe_2O_3.

Test the liquid which you have collected with blue litmus paper: it is strongly acid. Now add a little barium chloride to it: a white precipitate is formed. The liquid is an aqueous solution of sulphuric acid.

The changes which take place during the decomposition are rather complicated, but during the first stage what chiefly happens is the loss of the greater part of the water of crystallisation. At higher temperature the remaining water is driven off together with sulphur trioxide, and ferric oxide remains. Some absorption of oxygen from the air takes place during the heating.

Exp. 11. Action of Heat on Ammonium Sulphate, $(NH_4)_2SO_4$.—Introduce a small quantity of ammonium sulphate crystals into a test-tube and heat gently. The crystals crackle and fly about, and then melt. White fumes are evolved having a strong smell of ammonia, the presence of which may be confirmed by means of moist red litmus paper. After a time a white crystalline sublimate forms on the sides of the tube, terminated at its lower end, *i.e.* where the tube is hotter, by an oily liquid. Also a molten residue remains in the bottom of the tube.

Now discontinue the heating and allow the tube to cool. The liquid residue in the bottom solidifies to a white solid; so also does the oily layer which collected a little way up the sides. Break the tube and remove the solid in the bottom. You will note that it is rather hard. Introduce it into a test-tube and shake up with water. It dissolves. Test the solution with blue litmus paper: it is strongly acid. Add excess of caustic soda solution and warm: a strong smell of ammonia is observed.

This hard residue, which melts on heating and is soluble in water, forming an acid solution, is ammonium bisulphate, or ammonium hydrogen sulphate, NH_4HSO_4. The white sublimate in the tube consists of the same substance, and the oily layer at the base of the sublimate is merely the same salt in the liquid condition. It is formed from

the normal sulphate on heating by the loss of ammonia (which you have identified) according to the equation

$$(NH_4)_2SO_4 = NH_4HSO_4 + NH_3.$$

Exp. 12. Action of Heat on a Mixture of Sodium Carbonate, Na_2CO_3, and Calcium Sulphate, $CaSO_4$.—Grind up 1 gram of gypsum* (calcium sulphate) in a mortar to a fine powder, and then mix it thoroughly with 4 grams of anhydrous sodium carbonate. Introduce the mixture into a porcelain crucible, support this on a pipe-clay triangle, and heat over a Bunsen flame for twenty minutes to half an hour. Allow to cool and then heat the crucible in water in a porcelain dish to remove the contents. You will find that only part of the residue dissolves. Filter, and wash the residue with hot distilled water till a few drops of the filtrate, collected separately, give no effervescence with hydrochloric acid, showing that all soluble carbonate has been washed out.

Now transfer the insoluble residue to a test-tube and add dilute hydrochloric acid to it. The greater part of the solid dissolves with effervescence of gas, which you can prove to be carbon dioxide by holding a drop of lime water on the end of a glass rod in the tube: the lime water becomes milky.

The explanation of these results is that when calcium sulphate is fused with excess of sodium carbonate, the greater part of it is converted into calcium carbonate, with simultaneous formation of sodium sulphate, according to the equation

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

Calcium carbonate being insoluble in water remains on the filter along with any unchanged calcium sulphate (which is only slightly soluble in water), when the product of the fusion is filtered after boiling out with water. When the residue is treated with hydrochloric acid, the calcium carbonate dissolves with liberation of carbon

* Precipitated calcium sulphate may be used if available.

dioxide and formation of calcium chloride, as expressed in the equation

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

The unchanged calcium sulphate remains undissolved (unless a large excess of hydrochloric acid is used).

Exp. 13. Action of Heat on a Mixture of Sodium Nitrite, $NaNO_2$, and Ammonium Chloride, NH_4Cl. — Powder about equal proportions of sodium nitrite and ammonium chloride together in a mortar, dissolve in the least possible quantity of water, and heat gently in a test-tube. A colourless gas is steadily evolved. Pass a little into lime water—no milkiness is produced. Apply a light to the mouth of the tube—it is extinguished and the gas does not burn. Also it has no taste or smell. It is *nitrogen*.

The sodium nitrite and ammonium chloride first undergo double decomposition with formation of ammonium nitrite and potassium chloride. The former then decomposes into nitrogen and water. The equations representing the changes which take place are

$$NH_4Cl + NaNO_2 = NaCl + NH_4NO_2,$$
$$NH_4NO_2 = N_2 + 2H_2O.$$

Exp. 14. Action of Heat on a Mixture of Cupric Oxide, CuO, and Charcoal.—Grind up a little cupric oxide (black oxide of copper) with about a sixth part of its weight of charcoal in a small mortar. Heat the mixture in a test-tube or, better, a hard glass tube, fitted with a cork and delivery tube, and pass any gas evolved through a little clear lime water. The liquid is rapidly turned milky, showing that carbon dioxide is being evolved.

After heating strongly for some time, shake out the contents of the tube into a mortar. Observe the change in colour. Rub well with a pestle and note that some of the particles can be readily burnished and have a distinct red colour. To a portion of the changed powder add a few drops of dilute nitric acid. Reddish-brown fumes (nitrogen peroxide) are evolved.

Evidently the residue is metallic copper, which has been produced by the reduction of the black oxide with char-

coal, the latter being simultaneously oxidised to carbon dioxide, as expressed in the equation

$$2CuO + C = 2Cu + CO_2.$$

Exp. 15. Action of Heat on a Mixture of Calcium Sulphate, $CaSO_4$, and Charcoal.—Grind up a little calcium sulphate (either gypsum or the precipitated sulphate) with three or four times its bulk of charcoal. Heat the mixture in a test-tube closed at one end, and fitted with a cork and delivery tube. Allow the latter to dip into some lime water. This soon becomes milky, showing that carbon dioxide is being evolved.

After heating for some time, allow the tube to cool and pour onto the black residue a little dilute hydrochloric acid. Note the characteristic smell of sulphuretted hydrogen.

The change which takes place during the heating is the reduction of calcium sulphate to the sulphide, CaS, by the charcoal, which is simultaneously oxidised to carbon dioxide according to the equation

$$CaSO_4 + 2C = CaS + 2CO_2.$$

Calcium sulphide is decomposed by dilute hydrochloric acid with liberation of sulphuretted hydrogen and formation of calcium chloride as represented by the equation

$$CaS + 2HCl = CaCl_2 + H_2S.$$

Exp. 16. Action of Heat on Coal and Wood.—Fit up the apparatus shown in Fig. 7. *A* is a dry hard glass tube half-filled with *dry* coal dust. Before heating this tube it must be shaken to make an air-space over the coal dust. The wide test-tube *B* should be almost completely immersed in a beaker of cold water. The corks must fit tight. Heat the tube carefully. Note the formation of brown fumes; these mostly condense in *B*, and a liquid

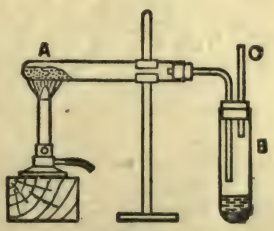

Fig. 7.

collects, which separates into two layers. Test the gas issuing at *C* with paper moistened with lead acetate solution; note the blackening, showing the presence of *sulphur* compounds. Hold a drop of lime water on the end of a glass rod in the gas: it becomes milky, proving that carbon dioxide is present.

After some time apply a light* to the gas at *C*; it burns with a luminous flame: it is *coal gas*. When the flame goes out, disconnect the apparatus. Test the light-coloured upper layer of liquid in *B* with red litmus paper: the litmus is turned blue. This upper layer is an aqueous solution of ammonia and ammonium salts (chiefly the sulphide and carbonate) and is called *gas liquor*; the thick dark brown lower layer is *coal tar*. Now break the tube *A* and note the hard *coke*.

The experiment may be repeated, using wood splints (*e.g.* match stalks) instead of coal dust. You would note the formation of a water distillate (which is *acid* to litmus), tar, inflammable gas and charcoal. The gas contains practically no sulphur compounds, but carbon dioxide is present, as in the case of coal. The watery distillate contains only a little ammonia (there is much less nitrogen in wood than in coal); the acid reaction is due to the presence of *acetic acid*.

* It will be safest first to test whether the air has been completely displaced from the apparatus by collecting a small test-tube of the gas (*C* should reach nearly to the end of the tube during this process) and applying it mouth downwards to a Bunsen flame. A "pop" or slight explosion shows that air is still mixed with the gas. Wait a short time and test again. When the gas burns quietly you may safely apply a light at *C*.

PART II.

QUANTITATIVE ANALYSIS.

CHAPTER I.

SIMPLE QUANTITATIVE EXPERIMENTS MAINLY GRAVIMETRIC.

1. On Weighing.—In performing the experiments to be described in the following pages we shall find it necessary to weigh bodies accurately. The quantities used are, as a rule, small, hence the need for a very delicate balance (see Fig. 8) and a good set of weights (see Fig. 9). A beam is poised at its centre on a knife-edge, and has at each end a similar knife-edge on which is balanced a pan. When the balance is not being used the beam and pans are supported on rests, but when we wish to weigh, we place the object to be weighed on one pan and the weights on the other, and by *gently* turning a metal axle cause the long needle attached to the beam to swing across a small ivory scale. If the needle swings to points at equal distances from the zero of the scale, the object and the weights are of equal mass, and the process of weighing has been accomplished.

Our first business is to see that the needle swings equal distances from the zero of the scale when the pans are unloaded; to ensure which the screw at the end of the right arm of the beam must be adjusted if necessary. As a rule this adjustment should only be made by one with some practical knowledge of the balance.

Having proved the balance to be in equilibrium about its zero reading, we place the object to be weighed on the left pan, take the largest weight from the box, and place it on the right pan (using a pair of forceps). Next we *slowly*

Fig. 8.

turn the axle and allow the beam to swing. The needle probably moves at once to the left and shows no tendency to swing back. This indicates that the right pan is too heavy. Turn the axle back to its first position

(*always* do this before adding or removing a weight) and try the next weight, replacing the first. At length we shall find a weight which is too light, the one before it having been too heavy. Keep the light weight still on the pan and place beside it the next smaller one. If these are too heavy, remove the smaller one and try still smaller ones in succession. We shall gradually work down from the grams to the decigrams, then to the centigrams, and finally to the milligrams.

As we get to the smaller weights, we must allow the needle to swing once or twice to each side before taking the readings. (If we read first, say, on the left, we must take the *next* reading on the right.) At last we shall find that a certain weight on the right pan is too large, whilst a milligram less makes it too small. The actual weight obviously lies between these, but for our purpose it will be sufficiently accurate to take the weight which gives the nearest approach to equal swings on each side of the zero.

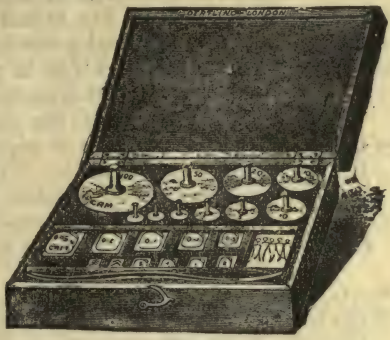

Fig. 9.

Now we count up the gram weights on the pan, write the total down, then count up the decigrams, centigrams, etc., in order. Having written down the weight of the object, we restore the weights to the box, checking them over to see if the total agrees with the weight we have noted down. This precaution is very necessary, especially to beginners—it prevents many erroneous weighings which would simply undo all the other work of the experiments.

Articles with any liquid attached to them should never be placed on the pans; loose substances should always be weighed in glass vessels, *e.g.* beakers, watch glasses, etc.;

no crucible, tube, etc., should be weighed when hot. It is advisable to have a small camel's-hair brush for removing dust from the pans and weights. A pair of forceps is usually provided with each box of weights for lifting them from the box to the pan, etc. Weights should never be lifted with the fingers. As the student becomes more practised he will be able to save much time in weighing, by choosing a weight somewhere near that of the object instead of working down from the largest in the box.

Use of a rider.—In order to avoid using weights below a centigram it is usual to have each arm of the balance-beam graduated into tenths. A small piece of platinum wire shaped as shown in Fig. 10 and called a *rider* is hung on the beam in any required position. The weight of the rider is one centigram, and if it is placed on the extreme graduation of the beam just above the point of suspension of the scale pan, the effect is the same as if a centigram weight had been placed in the pan. If, however, it is place on the first of the ten graduations its effective weight is only one-tenth of a centigram, *i.e.* a milligram, if on the second graduation the effective weight is two milligrams, and so on. Thus it is possible by suitably adjusting the position of the rider to weigh correct to a milligram.*

Fig. 10.

The adjustment of the rider is effected by means of a sliding brass rod which passes through the balance case. The rod carries a hook, which enables the rider to be picked up from the beam and transferred to another point; when not in use the rider hangs on the hook.

2. Use of Desiccator.—It is necessary, in all quantitative operations involving weighing, that everything be kept quite dry, for vessels, and especially finely divided substances, if left about, take up moisture from the surrounding air, and become in consequence heavier, sometimes in a marked degree.

* By estimation it is of course possible to weigh to a fraction of a milligram, and in the better balances the tenth divisions are subdivided further into hundredths.

For this reason, the air of the balance case is kept dry by placing inside it a vessel containing strong sulphuric acid or calcium chloride. Further, a dry air chamber called a *desiccator* is employed in which to keep the vessel and substance while they are cooling (they must never be weighed till quite cold). One form of desiccator is depicted in Fig. 11. It consists of a glass vessel divided into two compartments communicating with one another, and provided with a lid. The upper compartment contains a pipeclay triangle, the wires of which are bent at right angles so as to form legs. This stands on a piece of wire gauze, which covers the hole between the two compartments. Crucibles, etc., can be placed on the triangle to cool. The lower compartment contains granular calcium chloride, which keeps the air in the apparatus dry.* Instead of calcium chloride lumps of pumice soaked in conc. sulphuric acid may be used, and sometimes for special purposes pieces of caustic potash.

Fig. 11.

3. Determination of the Percentage of Carbon Dioxide contained in Calcium Carbonate by Ignition.—When calcium carbonate is strongly ignited it loses carbon dioxide and becomes converted into calcium oxide or lime. Take a small porcelain crucible and lid (platinum is better if it can be had), clean thoroughly, and heat to redness on a pipeclay triangle over a Bunsen flame, as shown in Fig. 12 (the lid should be removed occasionally for a few seconds with a pair of clean crucible tongs to allow water vapour to escape). Remove the flame and allow to cool partially. While still warm,

Fig. 12.

* It will be assumed that in all the experiments which follow the cooling is performed in a *desiccator*.

transfer to a desiccator and allow to cool completely for fifteen minutes or longer.*

Weigh the crucible accurately, and then bring into it about half a gram of pure precipitated calcium carbonate, heat gently over the Bunsen flame, but not to perceptible redness, to remove moisture, cool as before in the desiccator and weigh accurately again. The difference gives us the weight of carbonate taken. Now place the crucible on a triangle, with the lid almost covering the mouth, but leaving a small opening for the escape of carbon dioxide, heat it up to redness with a Bunsen flame, and then turn on a small blowpipe† flame. Gradually increase the supply of gas until you have the hottest flame possible, and heat with this for a quarter of an hour, then slowly diminish the flame, so allowing the crucible to cool down gradually. Transfer to the desiccator, cool for fifteen minutes, and again weigh accurately.

The contents will have diminished in weight owing to the loss of carbon dioxide, but may still contain undecomposed carbonate. To test whether this is the case or not, heat exactly as before, but only for five minutes, cool, and weigh again. If the further loss is only a milligram or so we can conclude that all the carbonate is practically decomposed, otherwise the heating, cooling, and weighing must be repeated till two consecutive weighings are the same within about a milligram. The difference between the final weighing, and the weight of the crucible, lid, and contents gives us the weight of the carbon dioxide contained in the weight of carbonate taken. Calculate from this the percentage of carbon dioxide.

The whole experiment should now be repeated and the mean of the two results taken.

This practice of carrying out experiments in duplicate and taking the mean should *always be followed*; in many

* It will be assumed that the process just described is gone through whenever the exact weight of an empty crucible is required.

† The *gas blowpipe* consists of two tubes, one within the other. Through the inner tube air is urged by means of a foot-blower, whilst gas is admitted to the annular space. Light the gas before starting the current of air.

cases a saving of time is effected by starting the two experiments together. In general if the results of the two experiments differ by more than one per cent. they are worthless.

Your results should be stated on the lines of the following example:—

Exp. 1. Wt. of crucible + lid = 11·431 gm.
" " " + chalk = 11·973 "

Wt. of chalk taken = 0·542 gm.

Wt. of crucible + lid + lime (1) = 11·742 gm.
" " " " (2) = 11·736 "
" " " " (3) = 11·735 "

The last two weighings only differ by 1 mg., and the weight may therefore be considered constant.

Wt. of crucible + lid + chalk = 11·973 gm.
" " " + lime = 11·735 "

Wt. of carbon dioxide evolved = 0·238 gm.

∴ Percentage of carbon dioxide in chalk

$$= \frac{0{\cdot}238}{0{\cdot}542} \times 100 \text{ or } 43{\cdot}9.$$

Exp. 2. Wt. of crucible + lid = 12·791 gm.
" " " + chalk = 13·347 "

Wt. of chalk taken = 0·556 gm.

Wt. of crucible + lid + lime (1) = 13·110 gm.
" " " " (2) } constant { = 13·105 "
" " " " (3) } { = 13·104 "
" " " + chalk = 13·347 "

Wt. of carbon dioxide evolved = 0·243 gm.

Percentage of carbon dioxide in chalk

$$= \frac{0{\cdot}243}{0{\cdot}556} \times 100 \text{ or } 43{\cdot}7.$$

Exp. 1 gave 43·9 per cent. of carbon dioxide.
Exp. 2 gave 43·7 per cent. of carbon dioxide.
The mean of these results is **43·8** per cent.

The theoretical percentage of carbon dioxide in chalk can be calculated from the equation which expresses the change taking place thus:

$$\underset{40+12+48^{*}}{CaCO_3} = \underset{=100}{CaO} + \underset{12+32}{CO_2}.$$
$$= 44$$

Obviously the percentage of carbon dioxide is **44**.

4. Determination of the Weight of Oxygen which Combines with one Gram of Magnesium.—Weigh a clean ignited porcelain crucible and lid. Cut off 30 cm. of *bright* magnesium ribbon (scrape the ribbon with a knife if it is not bright), roll it up *loosely* and place in the crucible; then weigh the whole. Fix securely on a pipeclay triangle and tripod. Heat the closed crucible sufficiently to cause the metal to burn when the lid is slightly raised. Do not let any white fumes escape. When the burning has nearly ceased remove the lid, but continue to heat for a few minutes longer. Cool and weigh the whole again. Now reheat for a short time, cool, and reweigh.

Repeat this process till the weight is constant. Then repeat the whole experiment.

The following example illustrates the method of stating the results:—

Exp. 1. Wt. of crucible + lid	=	10·138 gm.
„ „ „ + magnesium	=	10·341 „
Wt. of magnesium taken	=	0·203 gm.
Wt. of crucible + lid + magnesium oxide (1)	=	10·458 gm.
(2) } constant	=	10·473 „
(3) } constant	=	10·474 „
„ „ crucible + lid + magnesium	=	10·341 „
Wt. of oxygen	=	0·133 gm.

* See Appendix for a table of atomic weights sufficiently accurate for use in ordinary quantitative analysis.

∴ Wt. of oxygen which has combined with 1 gm. of magnesium $= \frac{0{\cdot}133}{0{\cdot}203}$ or 0·655 gm.

Exp. 2. Wt. of crucible + lid = 11·428 gm.
„ „ „ + magnesium = 11·659 „
Wt. of magnesium taken = 0·231 gm.

Wt. of crucible + lid + magnesium oxide (1) = 11·796 gm.
(2) = 11·806 „
(3) } constant = 11·811 „
(4) } = 11·811 „
„ „ crucible + lid + magnesium = 11·659 „
Wt. of oxygen = 0·152 gm.

Wt. of oxygen which has combined with 1 gm. of magnesium $= \frac{0{\cdot}152}{0{\cdot}231}$ or 0·658 gm.

The mean of the two experiments gives **0·657 gm.** as the weight of oxygen which unites with 1 gm. of magnesium. The calculated value is **0·658** gm. as shown below:—

$$2\,Mg + O_2 = 2\,MgO.$$
$$2 \times 24{\cdot}3 \quad 2 \times 16$$
$$= 48{\cdot}6 \quad = 32$$
$$48{\cdot}6 : 32 = 1 : 0{\cdot}658.$$

5. Determination of the Amount of Water of Crystallisation contained in Crystallised Copper Sulphate.—A portion of the water of crystallisation contained in copper sulphate is expelled at a temperature of 110°-115° C., but the remainder is held in much closer combination, and requires a temperature of about 250° C. for its complete explusion. We shall determine both the total amount of water in the salt and also that which is driven off at the lower temperature.

For this experiment a piece of apparatus called an *air-oven* or *air-bath* is required. This consists of a copper

chamber provided with a door and supported on legs at such a height that it can conveniently be heated by a Bunsen burner. There is a short funnel in the roof through which the hot air escapes, and a hole at the base of the door through which cold air enters to replace it; thus a gentle current of air is maintained through the oven. Frequently an adjustable ventilator takes the place of the hole in the door so that the air current can be regulated.

The temperature of the oven is registered by a thermometer which passes through a cork fixed in a second hole in the roof of the oven, and by carefully regulating the Bunsen flame it can be maintained practically constant at any desired point within certain limits. Since the floor and walls of the oven are at a considerably higher temperature than the interior, vessels must not stand on the floor or touch the walls; they are placed on a perforated shelf which rests on ledges at the sides of the oven (Fig. 13).

Fig. 13.

Purification of the Copper Sulphate.—Take about 20 gm. of ordinary copper sulphate crystals ("blue vitriol"), powder in a mortar, and then dissolve in the least quantity of boiling water. Filter the hot solution through a small filter paper placed, if possible, in a funnel surrounded by a hot-water jacket. Allow the clear liquid to run into a clean porcelain basin surrounded by cold water, and stir it rapidly with a glass rod. Fine crystals will separate out.

Pour off the mother liquor and place the fine wet powder on a watch glass inverted in a small funnel, in order to drain off as much of the liquid as possible. Press the drained crystals between blotting-paper, turning them frequently. Change the blotting-paper, and after pressing well and turning leave in a warm room for some hours. Preserve the crystals in a stoppered bottle.

Heat a small porcelain crucible, cool it in a desiccator,

and weigh. Add now about a gram of the crystals, after first powdering them finely, and weigh carefully again.

Take a pair of small clean watch glasses of the same size and dry them thoroughly. Also procure a clip of suitable size to hold them firmly together with the concave sides facing each other; the shape of the clip is shown in Fig. 14.

Place the watch glasses in the clip and weigh. Powder finely some of the copper sulphate crystals you have prepared and introduce about a gram into one of the watch glasses. Replace the glasses in the clip and weigh, so obtaining the weight of crystals taken.

Now separate the glasses again, and place them on the shelf of an air oven, raise the temperature of the oven to 110°-115° C. and keep it at this for half an hour. (The oven should be provided with a thermometer reading up to 300° C.) The powder will now appear white with a slight tinge of blue. Replace the watch glasses in the clip,* allow to cool in a desiccator and reweigh. (The clip should have been left in the desiccator during the heating of the glasses.)

Fig. 14.

Now separate the glasses again,† replace them in the oven, the temperature of which should still be at 110°-115° C., and heat for another quarter of an hour, the lid being off as before. Cool again in the desiccator and reweigh. If the weight is not practically the same as before continue the heating, cooling, and weighing until a constant weight is obtained.

Next place the watch glasses in the oven and raise the flame of the burner until the temperature reaches about 250° C. Keep it fairly steady at 250°-260° C. for about twenty minutes. Take out the glasses, place them in the desiccator for about fifteen minutes after clipping, and

* This should be done each time the glasses are cooled in the desiccator.

† This should be done each time the glasses are placed in the oven.

weigh again. Place again in the oven, which should still be at 250°-260° C. and heat for another quarter of an hour, cool as before and weigh. If the weight is practically constant all the water has been driven off; if not, repeat the heating, cooling, and weighing till a constant weight is attained.

The results are entered and the calculations made as illustrated in the example given below.

Wt. of watch glasses and clip		= 13·094 gm.
„ „ clip, and powdered crystals		= 14·089 „
„ crystals		= 0·995 gm.
Wt. of watch glasses, clip, and crystals after heating to 110°-115° C.		
	(1)	= 13·451 gm.
	(2) } constant	= 13·441 „
	(3) } constant	= 13·440 „
„ water expelled at 110°-115° C.		= 0·287 „
„ watch glasses, clip, and anhydrous copper sulphate (after heating to 250°-260° C.)	(1)	= 13·375 „
	(2) } constant	= 13·367 „
	(3) } constant	= 13·367 „
„ water expelled at 250°-260° C.		= 0·073 „
Total weight of water in the crystals		= 0·360 „

Now the molecular weight of copper sulphate, $CuSO_4$, is

$$63{\cdot}5 + 32 + 4 \times 16 = 159{\cdot}5,$$

and the molecular weight of water, H_2O, is

$$2 \times 1 + 16 = 18.$$

Hence if x represents the number of molecules of water of crystallisation contained in crystallised copper sulphate, we have

$$\frac{CuSO_4, xH_2O}{xH_2O} = \frac{159{\cdot}5 + x \times 18}{x \times 18} = \frac{0{\cdot}995}{0{\cdot}360}$$

$$\therefore x = 5{\cdot}02.$$

That is, crystallised copper sulphate contains 5 *molecules* of water of crystallisation, and its formula is $CuSO_4$, 5 H_2O. Of this water $\frac{0{\cdot}287}{0{\cdot}360} = \frac{4}{5}$ is expelled at 110°-115° C., *i.e.* 4 *molecules*.

The method adopted in the preceding experiment is of general application. As a further exercise the amount of water of crystallisation in crystallised barium chloride, $BaCl_2$, 2 H_2O, may be determined.

6. Determination of the Percentage of Iron contained in Ferrous Ammonium Sulphate.

Preparation of Ferrous Ammonium Sulphate, $(NH_4)_2SO_4$, $FeSO_4$, 6 H_2O.—Take about 50 gm. of good ferrous sulphate crystals and 25 gm. of ammonium sulphate—mix well and powder in a mortar, then dissolve in the least possible quantity of warm water. Filter into a clean basin, observing the same precautions as in preparation of pure copper sulphate described in the previous article, drain the fine crystals and dry between blotting-paper as there described. The substance, if kept in a well-stoppered bottle in the dark, keeps much better than ferrous sulphate.

Heat, cool, and weigh a small porcelain crucible and lid. Add about 0·3-0·4 of a gram of the dry substance prepared above and finely powdered and weigh exactly again. Place the crucible on a pipeclay triangle, so adjusting the lid that there is a very small opening between it and the edge of the crucible. Bring under it a small Bunsen flame, fixing the triangle about 6 in. above. Heat the contents of the crucible gradually, so that no spurting occurs from the sudden expansion of the water in the crystals. When the greenish colour has disappeared, being replaced by a dirty white, increase the supply of gas slightly; white fumes will be slowly evolved, due to the escape of ammonia and sulphur trioxide.

On more strongly heating the residue the white colour will be replaced by a brown, showing that the ferrous sulphate is being decomposed, leaving reddish brown ferric oxide. Heat up to bright redness, remove the lid so that the contents of the crucible can become thoroughly oxidised, and continue the heating for about ten minutes. Cool and

weigh. Repeat the heating for another ten minutes, cool, and weigh again. (Of course the lid should also be strongly heated in order to decompose any sulphate that may have been spurted on to it.) If the weighings do not differ by more than a milligram or so, we can assume that the experiment is completed.

The difference between the first and final weighings gives us the amount of ferric oxide present. $\frac{7}{10}$ths of this is the amount of iron contained in the sulphate, for

$$Fe_2O_3 = 2 \times 56 + 3 \times 16 = 160,$$
$$2\,Fe = 2 \times 56 = 112,$$

and $\frac{112}{160} = \frac{7}{10}$.

The following is an example of the determination:—

Wt. of crucible + lid	= 14·562 gm.
" " " + sulphate	= 15·094 "
Wt. of sulphate taken	= 0·532 gm.

Wt. of crucible + lid + Fe_2O_3 (1)	= 14·671 gm.
" " " " (2) constant	= 14·670 "
Wt. of ferric oxide	= 0·108 "

Amount of iron contained in this weight of oxide

$$= \tfrac{7}{10} \times 0{\cdot}108 \text{ or } 0{\cdot}076 \text{ gm.}$$

$$\text{Percentage of iron} = \frac{0{\cdot}076}{0{\cdot}532} \times 100 \text{ or } \mathbf{14{\cdot}3} \text{ per cent.}$$

The theoretical percentage of iron is **14·3**, as shown below:—

$$Fe(NH_4)_2(SO_4)_2.6\,H_2O$$
$$= 56 + 2(14 + 4) + 2(32 + 4 \times 16) + 6 \times 18$$
$$= 392.$$

$\therefore$ Percentage of iron $= \frac{56}{392} \times 100$ or 14·3.

The change which takes place on heating the double salt may be represented approximately by the following equation:—

$$4\,Fe(NH_4)_2(SO_4)_2.6\,H_2O + O_2$$
$$= 2\,Fe_2O_3 + 8\,NH_3 + 8\,SO_3 + 28\,H_2O.$$

7. Estimation of the Percentage of Carbon Dioxide contained in a Carbonate.

(*a*) *By determination of the loss of weight on treatment with an acid.*—Let us use calcium carbonate as the carbonate and hydrochloric acid as the acid.

Fig. 15.

Take a small wide-mouthed bottle and fit it with a rubber cork carrying a drying tube filled with granulated calcium chloride and with a glass tube reaching nearly to the bottom of the bottle (see Fig. 15).

Introduce some pure precipitated calcium carbonate into a small stoppered bottle called a *weighing bottle* (Fig. 16). Wipe off any chalk adhering to the mouth of the bottle, insert the stopper and weigh. Shake out about a gram of chalk into the flask, gently tap the bottle on the neck of the flask to shake the remaining chalk down again, and then carefully insert the stopper. During the whole of this operation *keep the mouth of the bottle over the mouth of the flask* to prevent any loss of chalk.

Fig. 16.

Now reweigh the bottle; the difference between the two weighings gives the weight of chalk taken. Pour water into the bottle till the chalk is well covered (do not add too much water).

Next tie a piece of cotton underneath the rim of a small test-tube, nearly fill the tube with strong hydrochloric acid, and lower it into the bottle. Then, without leaving hold of the cotton, insert the cork, so arranging that when the cotton is held tight by the cork the tube is in the position shown in the figure. See that the end of the straight tube dips in the liquid.

Now carefully weigh the whole. Then manipulate the bottle so that a *little* acid escapes from the small tube on to the chalk. Carbon dioxide is evolved, and first drives air out of the flask through the calcium chloride tube (its only exit); after a time the gas itself passes out. Any moisture carried away by the escaping gases is retained by

the calcium chloride, and so loss in weight is prevented. (If, however, the action is allowed to proceed *too rapidly* the drying will not be carried out effectively.) When the action slackens, upset a little more acid, and continue to do this from time to time till all the chalk has disappeared.

The flask is now full of carbon dioxide, and, further, some of the gas is dissolved in the liquid. Warm the flask carefully till it is so hot that you can barely hold it (*do not boil the liquid*). Now attach a piece of rubber tubing to the calcium chloride tube and suck *gently* till the pungent taste of carbon dioxide ceases to be noticed. The flask is now full of air again. Allow it to stand till it becomes quite cold and then reweigh.

Suppose the following results were obtained:—

Wt. of flask + chalk	= 10.32 gm.
„ „ alone	= 9·135 „
Wt. of chalk taken	1·185 gm.

Wt. of apparatus before the reaction	= 35·61 gm.
„ „ after „ „	= 35·085 „
Wt. of carbon dioxide evolved	0·525 gm.

We have then

0·525 gm. of carbon dioxide is evolved from 1·185 gm. of chalk.

$\therefore \frac{0{\cdot}525}{1{\cdot}185} \times 100$ or 44·5 gm. of carbon dioxide are evolved from 100 gm. of chalk.

The percentage loss is therefore 44·5 per cent.

We have seen in § 3 that the calculated percentage of carbon dioxide in chalk is 44 per cent. The change which takes place is represented by the equation

$$\underset{100}{CaCO_3} + 2\,HCl = CaCl_2 + H_2O + \underset{44}{CO_2}$$

(*b*) *By measurement of the volume of carbon dioxide evolved on treatment with an acid.*—In this experiment we will use sodium bicarbonate as the carbonate and dilute sulphuric acid as the acid.

Procure a 50 c.c. burette* and grease the tap well. Since the burette is not graduated right up to the end the volume from the 50 c.c. graduation to the closed end must be determined. For this purpose pour water into the burette by means of a small funnel till it stands at the 50 c.c. graduation. Run this water through the tap into a weighed beaker and reweigh. The difference between the two weighings is equal to the weight of the water. This measured in grams is numerically equal to the volume of the burette up to the 50 c.c. graduation, since one gram of water occupies 1 c.c. (practically).

Suppose you obtained the following results :—

Weight of beaker = 12·73 gm.
" " " + water = 17·93 "
Weight of water 5·20 gm.

Then 5·2 c.c. is the volume of the burette from the closed end to the 50 c.c. graduation. Write this volume down on a small piece of gummed paper and fasten it on to the burette below the 50 c.c. graduation.

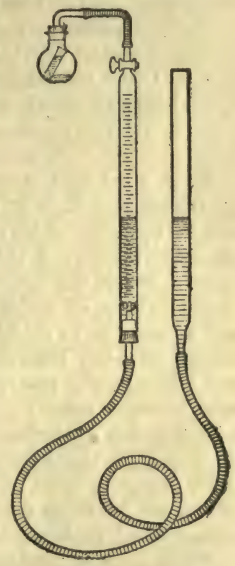

Fig. 17.

Now close the open end of the burette with a well-fitting rubber cork carrying a short piece of glass tubing. Next obtain a glass tube of about the same diameter and length as the burette and narrowed at one end. Take about 1½ metres of rubber tubing and wire the ends firmly on to the short glass tube of the burette and the narrow end of the other tube (which we will call the *pressure tube*).† Support the burette (inverted) and pressure tube close together in a vertical position, as shown in Fig. 17, by means of a retort stand and clamps.

* See page 74 for a detailed description of a burette.

† A second burette may be used as the pressure tube.

Now fill the burette *completely* with water by pouring the liquid into the pressure tube (which should be raised about 60 cm.*) till it just reaches the stopcock. The stopcock is then closed, and the pressure tube lowered and clamped.

Next weigh out into a small wide-mouthed flask about 0·15 gm. of sodium bicarbonate. Dissolve this in a little water and carefully introduce a small tube nearly filled with moderately dilute sulphuric acid (3 vols. of water to 1 vol. of concentrated acid), leaning it up against the side of the flask. Close the flask with a cork carrying a short delivery tube bent at right angles and connect this up to the burette by means of a short piece of rubber tubing (Fig. 17).

Now open the stopcock and upset the acid on to the bicarbonate a little at a time. Gas collects in the burette which consists chiefly of air driven out by the carbon dioxide, though a little carbon dioxide † may also pass over. When the action is complete, as shown by the fact that the level of water in the burette ceases to fall, allow the apparatus to stand till the water level in the burette ceases to *rise*, showing that the apparatus has regained the atmospheric temperature, and in the meantime hang a thermometer near the burette. Now adjust the pressure tube till the water level is the same as that in the burette. The gas in the burette is then at atmospheric pressure. Now read the level of water in the burette. (This must, of course, be done *upside down*, but no difficulty should be experienced in doing this.)

Suppose the reading is 12·2 c.c. Then the volume of gas collected is

$$5{\cdot}2 + 50 - 12{\cdot}2 \text{ or } 43{\cdot}0 \text{ c.c.}$$

Also read the temperature indicated by the thermometer, say 14° C., and the barometric pressure, say 740 mm. of mercury.

* This is in order that a space may ultimately oe left in which the water displaced by carbon dioxide may collect.

† The slight error introduced owing to the solubility of carbon dioxide in water may be avoided by using mercury in the apparatus.

The volume of gas collected must now be reduced to standard temperature and pressure, allowance being made for the fact that it is saturated with aqueous vapour.* Now the pressure of aqueous vapour at 14° C. is 12 mm. of mercury. (See Table, Appendix II.) We have then

43·0 c.c. of carbon dioxide, measured at 14° C. and 740 mm. of mercury, become

$$43{\cdot}0 \times \frac{273}{287} \times \frac{740 - 12}{760} \text{ or } 39{\cdot}2 \text{ c.c.}$$

measured at 0° C. and 760 mm. of mercury.

Now 1 c.c. of hydrogen measured at 0° C. and 760 mm. of pressure weighs 0·00009 gm.

Also the molecular weight of carbon dioxide is

$$CO_2 = 12 + 2 \times 16 \text{ or } 44.$$

∴ its relative density referred to hydrogen as unity is 44/2 or 22.

∴ 1 c.c. of carbon dioxide measured at 0° C. and 760 mm. pressure weighs

$$22 \times 0{\cdot}00009 \text{ gm.}$$

∴ 43·0 c.c. of carbon dioxide measured at 0° C. and 760 mm. pressure weigh

$$43 \times 22 \times 0{\cdot}00009 \text{ or } 0{\cdot}0851 \text{ gm.}$$

Suppose the weight of sodium bicarbonate taken was 0·164 gm. Then the percentage of carbon dioxide in the bicarbonate is

$$\frac{0{\cdot}0851}{0{\cdot}164} \times 100 \text{ or } 51{\cdot}9.$$

The decomposition of sodium bicarbonate by sulphuric acid is represented by the equation

$$\underset{84}{NaHCO_3} + H_2SO_4 = NaHSO_4 + H_2O + \underset{44}{CO_2}.$$

The calculated percentage of carbon dioxide is therefore

$$\frac{44}{84} \times 100 \text{ or } 52{\cdot}4.$$

* This aqueous vapour exerts a pressure, and for a *given temperature* this pressure has a *definite value* if the gas contains as much aqueous vapour as possible, *i.e.* is *saturated* with it.

8. Estimation of the Percentage of Oxygen in Potassium Chlorate.

(*a*) *By determination of the loss in weight on ignition.*—Weigh a small hard glass tube, place in it about 1 gram of potassium chlorate and weigh again. Heat carefully, holding the tube in a slanting position and rotating it constantly. The salt melts and then appears to boil. After a time the liquid gets thick, and when the gas evolution ceases a white and solid mass (potassium chloride) remains in the tube.

Weigh the tube again when cold. The loss in weight represents the weight of oxygen evolved.

Suppose that in an experiment the following results were obtained:—

Wt. of tube	= 15·613 gm.
„ „ tube + potassium chlorate	= 16·542 gm.
„ „ potassium chlorate	= 0·929 gm.
Wt. of tube and salt before heating	= 16·542 gm.
„ „ after heating	= 16·181 gm.
„ „ oxygen evolved	= 0·361 gm.

Then

Percentage of oxygen in potassium chlorate

$$= \frac{0{\cdot}361}{0{\cdot}929} \times 100 \text{ or } \mathbf{38{\cdot}9}.$$

Since potassium chloride is represented by the formula $KClO_3$, we have

$39 + 35{\cdot}5 + 3 \times 16$ or 122·5 gm. of the salt lose 3×16 or 48 gm. of oxygen on heating.

∴ Theoretical percentage of oxygen

$$= \frac{48}{122{\cdot}5} \times 100 \text{ or } \mathbf{39{\cdot}2}.$$

The weight of oxygen evolved on heating a known weight of nitre or red lead may be determined in a similar way.

(*b*) *By measurement of the volume of oxygen evolved on heating.*—Fit up an apparatus similar to that described in § 7 (*b*), but replace the small bottle by a hard glass tube containing about 1 gram of potassium chlorate (accurately weighed out). After filling the burette with water and lowering the pressure tube, as described in § 7 (*b*), attach the hard glass tube and heat the potassium chlorate. The oxygen evolved displaces the water from the burette.

When the level of water in the latter ceases to fall, allow the tube to cool to the temperature of the air. This will have happened when the level of water in the burette ceases to *rise*. Now make the levels of water in the burette and pressure tube the same. Read the volume of gas collected and the atmospheric temperature (by means of a thermometer hung near the burette) and pressure.

Reduce the volume to standard conditions, and then calculate the weight of this volume of oxygen. The calculation is similar to that in § 7 (*b*), the molecular weight of oxygen (O_2) being 32. Then, from the weight of oxygen evolved and the weight of potassium chlorate taken, calculate the percentage of oxygen in the salt.

9. Determination of the Chemical Equivalent of Copper by conversion into Black Copper Oxide.—Heat a crucible and lid; allow to cool, then weigh. Weigh out about a gram of pure copper foil (or wire) and place in the crucible. Remove to a fume closet, then pour upon the metal one or two drops of water, followed by a *few* drops of strong nitric acid. If necessary, add more acid to complete the solution of the foil. Gently evaporate down on a sand bath, taking care that there is no loss by spurting. The green powder left is copper nitrate.

Support the crucible on a pipeclay triangle and heat as strongly as possible until nothing but black copper oxide remains. Cool with the lid on, then weigh. Repeat the heating, cooling, and weighing till the weight is constant. From the results calculate the weight of copper which

combines with 8 gm. (*i.e.* the chemical equivalent) of oxygen; this gives the chemical equivalent of copper.

Example:—

Wt. of crucible + lid	= 10·392 gm.
„ „ „ + copper foil	= 11·463 „
Wt. of copper foil taken	= 1·071 gm.

Wt. of crucible + lid + copper oxide

(1)		= 11·751 gm.
(2)	constant	= 11·736 „
(3)	constant	= 11.735 „
„ „ „		= 10·392 „
Wt. of copper oxide formed		= 1·343 gm.

Wt. of oxygen which has combined with 1·071 gm. of copper is 1·343 − 1·071 or 0·272 gm.

Wt. of copper which would combine with 8 gm. of oxygen is

$$\frac{1{\cdot}071}{0{\cdot}272} \times 8 \text{ or } 31{\cdot}5 \text{ gm.}$$

The equivalent of copper is therefore **31·5**.

The value calculated from the formula CuO for black copper oxide is **31·8**, for Cu = 63·5 and O = 16.

∴ Ratio of copper to oxygen in CuO is 63·5 : 16 or 31·8 : 8.

10. Determination of the Chemical Equivalent of Copper by Deposition of the Metal.—A method by which the equivalent of a metal may be determined in some cases is the deposition of the metal from a solution of one of its salts by placing in it another metal. For instance, if metallic zinc or iron be introduced into a solution of copper sulphate, finely divided copper will be thrown down, and the amount deposited is equivalent to the amount of zinc or iron taken.

Choose two large test-tubes ("boiling tubes") such that one will just comfortably slide over the other. Break

each test-tube in half by making a scratch with a file and touching the scratch with a hot wire, when the tube will crack right round. Heat the rough edge of each tube in a Bunsen flame till the glass softens; then allow to cool.

Next fold a filter paper and fit it into a funnel. Remove it, roll it up, and introduce it into the smaller of the two tubes. Place the tubes separately in an air oven and regulate the temperature to about 110° C. After about half an hour remove them, close the smaller by sliding the larger over it (Fig. 18), allow to cool in a desiccator and weigh. Heat up again with the tubes separated, place them together again, allow to cool, and weigh. Repeat this process till the weight is constant.

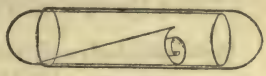

Fig. 18.

While the preceding process is going on weigh accurately a rather deep porcelain crucible of about 50 c.c. content. Into this bring about 35 c.c. of a solution containing not less than 3·5 grams of copper sulphate, and then about 0·4 gram of clean zinc foil, the exact weight of which has been determined. Warm *gently*. The zinc will slowly disappear, and a heavy powder will be precipitated to the bottom of the vessel. When on stirring with a glass rod there is no longer any sign of the foil, the reaction is complete. The zinc has replaced the copper in the salt originally taken, and we have now in the vessel metallic copper and a solution containing zinc sulphate and excess of copper sulphate.

Now place the weighed filter paper in a funnel, filter off the precipitate of copper, after first washing it by decantation, and wash on the filter with hot water till a drop of the wash water gives no blue coloration with ammonia. Finally wash with alcohol (rectified spirit) two or three times * and dry in the air oven. Next roll up the filter paper with the precipitate inside, place it in the tube, and

* Adhering water is thus removed and the time required for drying much shortened. This reduces the danger of error due to oxidation during drying.

weigh. Repeat the drying and weighing till the weight is constant. The increase in weight gives the amount of copper precipitated.

We have now

$$\frac{\text{Wt. of copper displaced}}{\text{Wt. of zinc used}} = \frac{\text{Equivalent of copper}}{\text{Equivalent of zinc}}.$$

Or taking the equivalent of zinc as 32·5,

$$\text{Equivalent of copper} = \frac{\text{Wt. of copper displaced}}{\text{Wt. of zinc used}} \times 32{\cdot}5.$$

The value obtained should be about 31·8.

Similarly, if a solution of nitrate of silver be substituted for that of copper sulphate, the equivalent of silver may be determined. In this case magnesium may be used in place of zinc, but the results are not satisfactory in the case of magnesium and copper sulphate.

11. Determination of the Equivalent of Magnesium by measuring the volume of hydrogen evolved on treatment with an acid.—Take a long measuring tube closed at one end and graduated in cubic centimetres; one graduated up to 100 c.c. is preferable. Take also a narrow beaker, pour in about half a litre of water, and add about 30 c.c. of concentrated sulphuric acid, stirring briskly. When the acid is cool fill up the tube completely with it, taking care that no air bubbles are allowed to enter; close the open end by means of the thumb, and invert in the beaker, which contains the greater portion of the diluted acid. Fix the tube in a small clamp stand.

Now procure a small tube about 4 cm. long and of such a diameter that it will slide comfortably into the graduated tube. Next scrape a piece of magnesium ribbon to remove all oxide, and weigh out a piece of about 0·1 gram (it should not be more). Drop the coiled ribbon into the small tube and fill up with water, shaking well, if necessary, to disengage any air bubbles. Close the end by means of the thumb, and bring it under the mouth of the graduated tube (which is still under the dilute acid). Force the small tube up into the wider one, and lower the latter un-

til it almost touches the bottom of the beaker and completely encloses the other (see Fig. 19). Remove your hand and rinse off the acid.

Soon the heavier acid will diffuse to the magnesium and begin to dissolve it. Hydrogen will be evolved, and will be collected in the tube. When the magnesium has completely dissolved, adjust the tube so that the liquid inside is level with that outside, more water being poured into the beaker if necessary. Do not touch the tube with your hand, but let it remain in the clamp, upon which hang a thermometer close to the tube in order to read the temperature of the air in the neighbourhood of the gas.

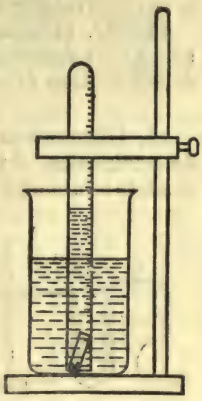

Fig. 19.

In a few minutes read the temperature, the barometric pressure and the volume of the gas (adjusting the tube again if necessary so that the levels of liquid inside and outside are the same). From these calculate the volume at 0° C. and 760 mm. pressure, making allowance for the fact that the gas is not dry, but is saturated with aqueous vapour. In making the correction, use the table given in Appendix II. Knowing that 1 c.c. of hydrogen under these conditions weighs 0·00009 gram, find the weight of the hydrogen collected.

Then—

$$\frac{\text{Weight of Magnesium}}{\text{Weight of Hydrogen}} = \text{Equivalent of Magnesium.}$$

The value obtained should be about 12.

The equivalents of zinc and iron may be determined in an exactly similar manner, using about 0·2 gram of bright zinc foil * in the former case and about 0·2 gram of fine

* Zinc in the form of foil is generally so pure that it is necessary to add a few drops of copper sulphate solution in order that it may dissolve in sulphuric acid.

iron wire (which has been scrubbed with a piece of sand-paper to remove rust) in the second case.

The same method may also be used in the case of aluminium (use 0·05 gram of the foil), but dilute hydrochloric acid must replace dilute sulphuric acid, which only attacks the metal very slowly. (Hydrochloric acid also acts more readily than sulphuric acid in the case of iron.)

Finally, in place of the apparatus you have just been using that described in § 7 (*b*) may be employed for the determination of equivalents by this method.

12. Illustration of the Law of Constant Proportion by determination of the Composition of Water.—Take a hard glass tube about 20 cm. long and 1·5 cm wide, and fit it with corks. Push into the tube a loose plug of asbestos (which has been previously ignited and allowed to cool in a desiccator) so that it is about a quarter of the way up the tube (A, Fig 20).

Fig. 20.

Weigh out, approximately, 5 gm. of finely-powdered black oxide of copper,* and introduce it into the tube at the end remote from the asbestos, by means of a small funnel. Now introduce a second plug of asbestos (ignited as before), carefully pushing it up the tube so that it sweeps along all particles of oxide. The distance between the two asbestos plugs should be about 6 cm. Place the tube horizontal and tap it so that the oxide forms an even layer with a free air space all along the tube. Carefully wipe off any oxide from the outside of the tube.

Next weigh the tube and copper oxide accurately. Also weigh a U-tube containing granular calcium chloride

* This should be previously heated to redness in air (to get rid of moisture, etc., attached to it), and, whilst still warm, introduced into the tube just before commencing the experiment.

and united with a horizontal bulb as shown in the diagram. Attach the U-tube and bulb to the straight tube as shown, arranging that the tube which passes through the cork *does not reach beyond it.** Connect the other end of the tube to a supply of hydrogen prepared by the action of dilute sulphuric acid on zinc, and dried by passing through a U-tube filled with granular calcium chloride. Allow the hydrogen to pass through the tube for a few minutes in order to displace the air. Test if the air has been removed by collecting a test-tube of the issuing gas and holding the tube mouth downwards to a Bunsen flame. If the gas burns with only a slight pop all the air has been driven out. Then heat the oxide of copper by means of a flat-flame burner.

The colour of the oxide will slowly change to a dark red, and water will condense in the further end of the tube and the horizontal bulb. The heating must be continued and the stream of hydrogen passed until no more traces of moisture are observed in the straight tube. You will find

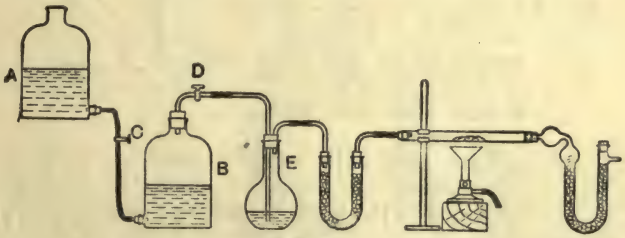

Fig. 21.

it necessary to warm the further end of the tube in order to drive out the water which collects there. Do this with an ordinary Bunsen burner, taking care that the tube does not become so hot as to affect the cork. Most of the moisture will now collect in the horizontal bulb, and the rest will be absorbed by the calcium chloride.

* If it did you would be unable subsequently to drive all the water out of the tube.

Now allow the apparatus to cool, still passing a slow current of hydrogen. When cold disconnect the hydrogen generating flask, leaving the calcium chloride tube in place. Now pass a slow current of dry air through the apparatus by means of the arrangement shown in Fig. 21.* The upper bottle A is filled with water, which flows down into B when the tap D and screw-clip C are open, and forces the air out through the exit-tube. The air is first passed through a small sulphuric acid wash-bottle E, which serves to indicate the rate of flow and also partially dries it. It then traverses the remainder of the apparatus (being further dried by the calcium chloride in the U-tube), and sweeps out the hydrogen.† The current of air is regulated by the tap and screw-clip, and should be maintained for about five minutes.

Reweigh the tube (+ copper) and the U-tube and bulb. We have now all the data necessary for calculating the ratio of hydrogen to oxygen in water.

Enter your results thus :—

grams.

Wt. of heating tube + copper oxide $= x$
„ „ „ + copper ... $= y$
„ oxygen which has been converted into water ... ... $= x - y$
„ U-tube and bulb before experiment ... ... $= a$
„ U-tube and bulb after experiment ... ... $= b$
„ hydrogen in the water formed $= b - a - (x - y)$

Hence—

Weight of oxygen united with 1 gm. of hydrogen is

$$\frac{x - y}{b - a - (x - y)}.$$

You should find this to be about 8 gm.

* A simpler way is to use a "*scent bottle*" *bellows.*

† If you weigh with hydrogen in the tubes instead of air, you will introduce errors ; for the previous weighings were made with air in the tube, and hydrogen is much lighter than air.

Repeat the experiment and show that you get the *same result*. Now try another oxide in place of copper oxide—say litharge; again the result will be the same.

Thus the Law of Constant Proportion, which states that *the same compound always contains the same elements united in the same proportion by weight*, has been illustrated in the case of water.

13. Illustration of the Law of Multiple Proportion by determination of the composition of Litharge and Lead Peroxide.—Weigh accurately into a small porcelain boat (*a*, Fig. 22) about a gram of lead peroxide (brown oxide of lead). Push the boat into a hard glass tube of about the

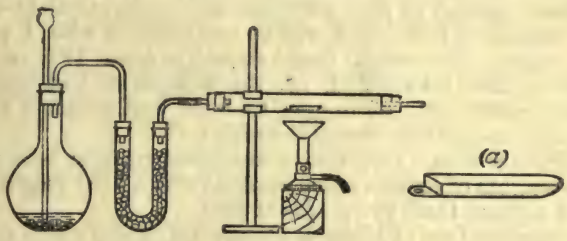

Fig. 22.

same size as that used in the previous experiment. Fit the tube with corks, carrying short pieces of glass tubing. Now connect one end of the tube with an apparatus for preparing dry hydrogen. Allow the hydrogen to pass through the tube for a few minutes to displace the air (test as usual). Then heat the boat gently by means of a flat-flame burner. The powder gradually changes colour, while *steam* passes out of the tube along with the unused hydrogen. When the cloud ceases and the powder has become quite black (*i.e.* changed into metallic lead) raise the boat to red heat for a few seconds to fuse the lead, while the current of hydrogen still passes. Cool, stop the current of hydrogen, withdraw the boat by means of a copper wire from the end of the tube attached to the

hydrogen apparatus (because there will probably be some drops of water at the other end) and reweigh it.

Enter your results thus:—

	grams.
Wt. of boat + lead peroxide	$= x$
„ boat	$= y$
„ boat + lead	$= a$
„ lead in oxide taken	$= a - y$
„ oxygen in oxide taken	$= x - a$

Therefore the weight of lead combined with one part by weight of oxygen in lead peroxide is $\frac{a-y}{x-a}$ grams.

Your result should work out at about 6·45 gm.

Now repeat the experiment, using litharge (yellow oxide of lead) instead of lead peroxide, and again calculate out the weight of lead which was in combination with 1 gm. of oxygen. The weight found should be about 12·9 gm.

Now $12{\cdot}9 : 6{\cdot}45 = 2 : 1$, *i.e.* the weights of lead which unite with 1 gm. of oxygen to form lead peroxide and litharge respectively are in the ratio 2 : 1.

There is then a very simple numerical relation between the weights of oxygen which combine with a fixed weight of lead to form these two oxides of lead.

Thus the Law of Multiple Proportion, which states that *when one element unites with another in more than one proportion the different weights of the one element which unite with a fixed weight of the other element bear a simple numerical relation to one another*, has been illustrated in the case of these oxides.

Another pair of oxides which may be used for this experiment is black oxide of copper (cupric oxide) and red oxide of copper (cuprous oxide)

CHAPTER II.—VOLUMETRIC.

I.—ACIDIMETRY AND ALKALIMETRY.

14. Equivalent Weights of Acids and Bases.—The alkalies turn red litmus blue, the acids turn blue litmus red, and if an alkali is added little by little to an acid, a point is reached at which the solution is *neutral*, that is, it produces no change either on red or blue litmus.

At this stage the alkali and acid have been brought together in the quantities necessary to form a neutral salt. What these quantities are may be learned by reference to such an equation as—

$$\underset{2(32+16+1)}{2\,NaOH} + \underset{2+32+4\times16}{H_2SO_4} = Na_2SO_4 + 2\,H_2O.$$
$$= 80 \qquad = 98$$

Taking the combining weights of the alkali and acid entering into this reaction, it will be seen that 80 parts of sodium hydroxide just suffice to neutralise 98 parts of sulphuric acid.

Some acids contain one atom of replaceable hydrogen; others, like sulphuric acid, contain two atoms; and others three. For the sake of uniformity the quantities dealt with in volumetric processes are always those which are *equivalent to one atom of hydrogen.* In the case of an acid this means that a quantity of the acid which contains *one replaceable atom of hydrogen* is taken, and this is spoken

of as the *equivalent weight* of the acid. In the case of a base the amount which will neutralise one equivalent weight of an acid is used, and this is spoken of as the *equivalent weight* of the base. Thus, since sulphuric acid is dibasic its equivalent weight is $\frac{98}{2} = 49$ gm. (taking 1 gm. of hydrogen as unity), and the quantity of caustic soda which neutralises this weight of acid is $\frac{80}{2} = 40$ gm. These are therefore the quantities of H_2SO_4 and NaOH used in making up solutions for volumetric analysis.

The equations

$$NaOH + HCl = NaCl + H_2O,$$
$$NaOH + HNO_3 = NaNO_3 + H_2O,$$

show that 40 gm. of caustic soda will neutralise 36·5 gm. of hydrochloric acid and 63 gm. of nitric acid respectively.*

Suppose we had made up the following solutions :—

(*a*) 1 litre to contain 40 gm. of caustic soda;
(*b*) 1 „ „ 49 „ sulphuric acid;
(*c*) 1 „ „ 36·5 „ hydrochloric acid.

It is evident that a certain volume (say 10 c.c.) of (*a*) will exactly neutralise the same volume of either (*b*) or (*c*), assuming, of course, that the solutions are uniformly mixed and so of the same strength throughout; for then the *weight* of each dissolved substance is proportional to the volume of the solution.

These solutions are now interchangeable and may be used as a means of estimating quantitatively the acidity (or alkalinity) of any given solution.

For instance, 50 c.c. of a solution A is taken: it is found to be *acid* and requires, say, 15 c.c. of (*a*) to neutralise it. The acid present is equivalent to that contained in 15 c.c. of (*b*) or (*c*). Or 50 c.c. of a solution B is taken and found to be *alkaline*, and to require say 12 c.c. of (*b*) to neutralise it. The alkali present is equivalent to that contained in 12 c.c of (*a*).

* The sign "$\equiv$" is often used to signify "is equivalent to," *e.g.* 40 gm. NaOH $\equiv$ 36·5 gm. HCl.

15. Standard Solutions.—A *standard solution* is one the *exact strength* of which is known.

Normal and Decinormal Solutions.—When the quantity of a substance dissolved in a litre is the equivalent weight of the substance expressed in *grams*,* such a solution is known as a *normal* solution, and is designated N. Such solutions are generally too concentrated to be conveniently used in volumetric work, and it is usual to make up solutions of *one-tenth* this strength. These are known as *decinormal* solutions, and are designated $\frac{N}{10}$. In some cases it is desirable to employ even weaker solutions than these, and to prepare them of *one-hundredth* the normal strength. Such solutions are termed *centinormal* solutions, and are designated $\frac{N}{100}$.

A normal solution of NaOH contains 40 gm. to the litre.
A decinormal . „ „ „ 4 „ „
A centinormal „ „ „ 0·4 „ „

As an example of the use of such solutions in quantitative estimation, let us suppose that 100 c.c. of a solution is given containing caustic potash, and it is desired to ascertain the amount of potash in it. Suppose it is found that 20 c.c. of the solution requires 10·8 c.c. of decinormal acid to neutralise it. The 100 c.c. would thus require $10{\cdot}8 \times 5$ or 54 c.c. of decinormal acid.

But 54 c.c. of decinormal acid would be just neutralised by 54 c.c. of decinormal caustic potash.

Now $KOH = 39 + 16 + 1 = 56$.

$\therefore$ 1 litre or 1000 c.c. of decinormal caustic potash would contain $\frac{56}{10}$ or 5·6 gm. of KOH.

$\therefore$ 54 c.c. of $\frac{N}{10}$ caustic potash would contain

$$\frac{54 \times 5{\cdot}6}{1000} \text{ or } 0{\cdot}3 \text{ gm. of KOH.}$$

This is therefore the weight of KOH in 100 c.c. of the given solution.

* This weight is called the *gram equivalent* of the substance.

16. Measuring Vessels—Titration.—In order to carry out the operations of volumetric analysis we must provide ourselves with certain measuring vessels. Diagrams of these are given in Fig. 23.

A is a narrow glass tube provided with a tap at the lower end, and is called a *burette*. It is graduated, generally in tenths of a cubic centimetre, the graduations reading downwards (see enlargement of the upper part of the burette on the left of the diagram), so that the volume of liquid run out can be measured by reading the level of

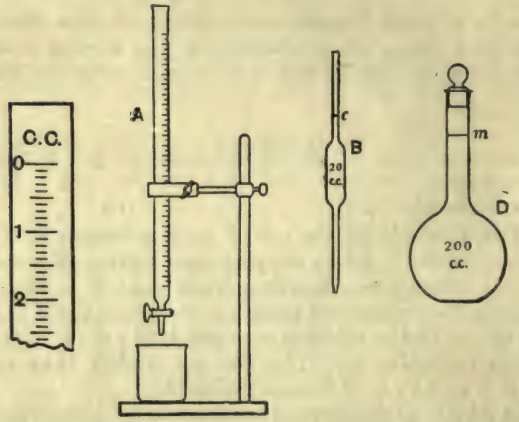

Fig. 23.

the liquid at the start and at the end of the operation. The burette is clamped in a vertical position to a wooden or iron stand, as shown.

B (Fig. 23) is called a *pipette*, and is a glass vessel by means of which a known small volume of liquid may be withdrawn from one vessel and transferred to another. The pipette is filled by suction * up to a mark (*c*) near the top and then contains exactly 20 c.c. of liquid. (Pipettes

* Be careful to avoid sucking the liquid into your mouth.

for measuring out other volumes, 50, 25, 10, or 5 c.c., are also made.) To prevent the liquid running out during transference, the upper end of the pipette must be closed with the thumb. The liquid is then delivered into a beaker or flask as required.

D (Fig. 23) represents a *measuring flask*. When filled up to the mark *m* it contains a definite volume of liquid (200 c.c. in this particular case). Measuring flasks are usually provided with ground glass stoppers.*

Readings of measuring vessels should not be hurriedly done, as the liquid requires a little time to drain down from the walls. The reading, especially of the burette, is liable to *parallax error*. The meaning of this will be understood by a reference to Fig. 24, which represents a portion of a burette. If the eye E is placed *level with the bottom of the meniscus* (*i.e.* the curved surface of the water—it is usual to read from the bottom of the curve) the reading is 23·6 c.c.; this is the correct reading. The eyes E_1 and E_2 are placed respectively above and below the meniscus, and the readings are 23·3 c.c. and 24·0 c.c.—*i.e.* errors of 0·3 c.c. and 0·4 c.c. are introduced.

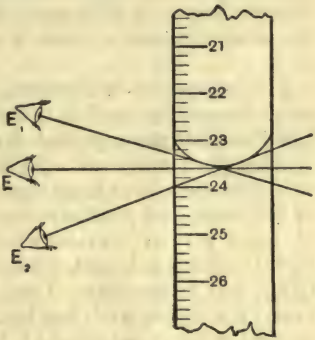

Fig. 24.

A piece of white paper held behind the burette is of assistance in taking a reading.

Parallax error is readily avoided in the case of the measuring flasks and pipettes because the graduation mark (*m* in D and *c* in B, Fig. 23) is scratched right round the glass so as to form a horizontal circle. If then the eye is so placed that the *circle* appears a *straight line*

* It should be noted that the measuring vessels used in volumetric work are seldom graduated quite accurately, but except for very accurate work the errors are negligible.

and the bottom of the meniscus *just touches the line*, the vessel is just filled to the graduation mark.

Suppose now we wish to find what volume of a given acid solution is required to neutralise 20 c.c. of a given solution of an alkali. 20 c.c. of the alkaline solution are measured out into a beaker or flask by means of a pipette, and two or three drops of litmus solution are added. The acid solution is then gradually run in from a burette till the blue colour of the litmus is *just* changed to red. The volume of liquid run out is the required volume of acid.

The operation is called *titration*, and the coloured substance (litmus in this case) that is used to indicate when the neutralisation is exact is called the *indicator*.

17. Indicators in Common Use.—*Litmus* is the indicator most commonly used in titrating acids and alkalis, but it has the disadvantage that it is affected by carbon dioxide. If, therefore, standard acid has been added to a carbonate, sufficient may have been used to combine with the whole of the base, and yet the reaction will be *acid* in consequence of some carbon dioxide which remains dissolved in the liquid. Such a liquid, when boiled (thereby expelling the CO_2), will be neutral. This difficulty can, indeed, be got over by working with hot liquid and boiling it when the neutral point is approached, but there is usually a sacrifice on the score of accuracy and of time.

Methyl orange is an indicator that is not affected by carbon dioxide, and in titrating in presence of carbonates it is unnecessary to boil the solution; indeed, this indicator should only be employed in cold solutions. Add only two or three drops of the indicator so that the (neutral or alkaline) solution has a *very faint* yellow colour, then the first drop of acid in excess gives a sharp change to a pink tint. Methyl orange cannot be used as an indicator in the case of organic acids.

Phenol phthaleïn is another indicator in common use. It is colourless in acid solution, and pink in alkaline solution. It cannot be used in titrating carbonates, as it is affected by carbon dioxide, but it can be employed for titrating

organic acids. Phenol phthaleïn cannot be used in the presence of ammonia.

Speaking generally, the quantity of indicator used should not exceed a few drops or the "end point" of the reaction will not be sharply defined.

18. Preparation of Decinormal Sulphuric Acid.—We have seen above that the equivalent weight of sulphuric acid is 49 gm. and that therefore the normal solution should contain 49 gm. H_2SO_4 per litre, and the decinormal 4·9 gm. The ordinary pure concentrated acid contains only about 95 per cent. H_2SO_4. Hence 5 gm. of this would contain rather less than the requisite amount for 1 litre.

Weigh out about 5·2 gm. of the pure acid in a small beaker. Pour the acid gradually (with shaking) into about $\frac{3}{4}$ of a litre of distilled water contained in an ordinary flask. Wash out the beaker with a little water, adding the washings to the flask. When the acid solution has cooled down to atmospheric temperature pour it into a graduated litre flask and make up to the mark with distilled water.

Such a solution will be approximately decinormal. Its strength must now be accurately ascertained. This is best accomplished by titration against a known weight of sodium carbonate.

19. Standardisation of Decinormal Sulphuric Acid.—Heat about 6 gm. of pure Na_2CO_3 or 10 gm. of pure $NaHCO_3$ (which on heating becomes converted into Na_2CO_3), till constant in weight, in a porcelain basin over the flame of a Bunsen burner, keeping it stirred from time to time with a glass rod. Cool in a desiccator. Introduce the salt into a weighing bottle and weigh out accurately rather more than 5 gm. of the salt into a litre flask. Introduce some water and shake up till the salt dissolves. Then fill up the flask to the mark with water and shake up so that the solution is of the same strength at all parts. The exact strength of this solution is known. Suppose, for example, 5·25 gm. of Na_2CO_3

were weighed out, then the solution contains 5·25 gm. Na_2CO_3 per litre.*

Measure out 20 c.c. of the solution into a beaker with a pipette, and add two or three drops of methyl orange.

Fill a burette† with the approximately decinormal sulphuric acid, read the height of the liquid, and run the acid into the beaker till the colour of the solution changes from yellow to pink. The first 18 c.c. or so can be run in rapidly, but after this, as the neutralisation point is approached, the liquid should be allowed to fall in a drop at a time, stirring after each addition.‡ To assist you in observing the change of colour, the beaker should be placed on a sheet of white paper during the titration. Read the height of the burette again. The difference between this and the first reading gives the volume of sulphuric acid required to neutralise 20 c.c. of the sodium carbonate solution.

Wash out the beaker, measure out another 20 c.c. of the sodium carbonate solution, and repeat the titration, running in all but the last ½ c.c. of sulphuric acid at once. Now make a third titration in a similar manner, and take the mean of the three results.

Let us suppose that the following were the observations made :—

Wt. of weighing bottle + Na_2CO_3	(1)	= 16·214 gm.
„ „ „ „	(2)	= 10·964 „
„ Na_2CO_3 taken		= 5·250 gm.

* The standard solutions you prepare should be preserved in suitable bottles ; Winchester quarts are very convenient.

† The stopcock of the burette should be well greased with vaseline. The burette should always be washed out with the solution to be used in the titration (sulphuric acid in this case) before filling. Of course if necessary it should be washed first with distilled water.

‡ Unless you have a very fair idea of the strength of the solution which is being titrated (as in this case), it is best to make a rough rapid titration first so as to get an approximate idea of the strength of the solution. Then make three accurate titrations and take the mean of them.

1st titration.—Height of burette (1) = 2·4 c.c.
„ „ (2) = 22·0 c.c.
Vol. of H_2SO_4 = 19·6 c.c.

2nd titration.—Height of burette (1) = 22·0 c.c.
„ „ (2) = 41·5 c.c.
Vol. of H_2SO_4 = 19·5 c.c.

3rd titration.—Height of burette (1) = 1·6 c.c.
„ „ (2) = 21·2 c.c.
Vol. of H_2SO_4 = 19·6 c.c.

The mean of the three titrations is 19·57 c.c.,* or 19·6 c.c. within the limits of accuracy of the experiment. This volume of H_2SO_4 neutralises, *i.e.* is equivalent to, 20 c.c. of the sodium carbonate solution, *i.e.* to 20 × 0·00525, or 0·105 gm. of Na_2CO_3. But from the equation

$$\underbrace{Na_2CO_3}_{2\times23+12+3\times16} + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$$
$$106$$

we see that 106 gm. of Na_2CO_3 are equivalent to 98 gm. of H_2SO_4.

∴ Weight of H_2SO_4 equivalent to 0·105 gm. of

$$Na_2CO_3 = \frac{98}{106} \times 0{\cdot}105 \text{ gm.}$$

This weight of sulphuric acid is contained in 19·6 c.c. of the solution.

$$\therefore \text{Weight of } H_2SO_4 \text{ in 1 litre} = \frac{98}{106} \times 0{\cdot}105 \times \frac{1000}{19{\cdot}6} \text{ gm.}$$
$$= 4{\cdot}95 \text{ gm.}$$

The solution is therefore somewhat stronger than

* *Note.*—If any two of the readings differ by more than 0·15 c.c. the experiment is worthless.

decinormal. It should be made accurately* decinormal by dilution as follows :—

1000 c.c. of decinormal sulphuric acid contain 4·9 gm. H_2SO_4.

$\therefore$ $1000 \times \frac{4{\cdot}95}{4{\cdot}9}$ or 1010 c.c. of decinormal sulphuric acid contain 4·95 gm. H_2SO_4.

$\therefore$ If 1010 − 1000 or 10 c.c. of water are added to the solution it will be accurately decinormal.

Add this volume of distilled water by means of a burette or pipette and mix the solution thoroughly by shaking. Label the solution 1 c.c. = ·0049 gm. H_2SO_4.

20. Discussion concerning the Volumes of Liquids used in Titration.—The question as to the most suitable volumes of liquids to use in volumetric analysis is an important one. If the volumes employed are too small the percentage error introduced by a slight experimental error becomes so large as to render the results valueless.

Suppose, for example, that only 3 c.c. of the liquid in the burette was required to bring about neutralisation and *one drop* too much or too little was run out. Now one drop measures about 0·05 c.c., so the error introduced amounts to $\frac{0{\cdot}05}{3} \times 100$ or more than $1\frac{1}{2}$ per cent. If 20 c.c. had been used an error of *two drops* would only have introduced a percentage error of $\frac{2 \times 0{\cdot}05}{20} \times 100$ or $\frac{1}{2}$ per cent.

For ordinary purposes the most convenient pipettes to use are those containing 20 or 25 c.c.; then since the liquids titrated are as a rule of about the same strength the quantity of liquid run in from the burette will also be about 20-25 c.c. If the liquids differ greatly in strength

* This is not strictly correct, because it is assumed that when, say, 100 c.c. of dilute acid is mixed with 10 c.c. of water, the volume of the resulting liquid is 100 + 10 = 110 c.c., whereas such is not the case. If, however, the volume of water added is *quite small*, no sensible error is introduced.

(as shown by a rough preliminary titration) the stronger one should be diluted down to about the strength of the other by measuring out a known volume and making up to a larger known volume; an accurate titration is then made, using the diluted solution. Suppose, for example, 100 c.c. of an acid solution of unknown strength are diluted to a litre and titrated with an alkali. Then the strength of the original solution is $\frac{1000}{100}$ or 10 times that of the diluted solution as determined by the titration.

21. Preparation of Decinormal Caustic Soda.—When assured of the accuracy of the decinormal solution of sulphuric acid, it may be used for preparing decinormal caustic soda (or potash or ammonia), on the assumption that equal volumes of the two solutions should exactly neutralise one another.

Weigh out rather more than 4 grams of pure caustic soda stick, dissolve in water and make up to a litre. Estimate the strength of the solution by means of the decinormal sulphuric acid, using litmus as indicator. Measure out 20 or 25 c.c. of the caustic soda into a beaker, add a few drops of litmus solution, and run in the acid from a burette till the colour becomes distinctly red.

The strength of the caustic soda solution should be rather greater than decinormal. If not, add more solid NaOH and estimate the strength again. Now make the solution accurately decinormal by dilution, calculating the amount of water required, as in the case of sulphuric acid (above).

22. Preparation of Decinormal Hydrochloric Acid.—Measure out 15 c.c. of pure concentrated hydrochloric acid (using a burette) and make up to a litre. This solution will be approximately decinormal. Estimate its exact strength by means of the decinormal caustic soda solution you have prepared, using methyl orange as indicator. Make the solution accurately decinormal as in the previous cases (HCl = 1 + 35·5 or 36·5, ∴ 1 lit. of $\frac{N}{10}$ hydrochloric acid contains 3·65 gm. HCl or 1 c.c. contains ·00365 gm. HCl).

In order to test the accuracy of your work determine the strength of this $\frac{N}{10}$ hydrochloric acid by means of your standard sodium carbonate solution as you did in the case of $\frac{N}{10}$ sulphuric acid; use methyl orange as indicator.

23. Correction Factor for the above Solutions.—Although it very much simplifies the calculations to be made if the solutions are accurately normal, decinormal, or centinormal, as the case may be, yet it is not at all easy to accomplish this in practice. Substances like the caustic alkalies cannot be accurately weighed owing to the rapidity with which they take up moisture and carbon dioxide from the air, nor can the acids be obtained and weighed so as to correctly estimate the actual amount of acid taken.

Moreover, if, by the above processes, solutions are obtained approximately of the strength stated, they are not readily brought to the exact strength, for the reason stated in the footnote on p. 52. When, therefore, approximately normal, decinormal, etc., solutions are obtained, the exact strength must be ascertained by the means already stated, and a *correction factor* may then be determined, which is written on the label attached to the bottle, and which must be taken into account whenever calculations are made from the results of an experiment.

Suppose, for instance, that the sulphuric acid is found to contain 4·95 gm. of H_2SO_4 instead of 4·9 gm. It is stronger than decinormal in the proportion $\frac{4{\cdot}95}{4{\cdot}9}$ or 1·01. The factor 1·01 is stated on the bottle, and the number of cubic centimetres used in the titration, when multiplied by this, gives the number of cubic centimetres that would have been required had the solution been strictly decinormal. Or instead of this the exact strength of the solution may be stated on the bottle; *e.g.* 1 c.c. = ·00495 gm. H_2SO_4 in the case under consideration. This is perhaps on the whole the most satisfactory plan.

24. Preparation of Normal Oxalic Acid.—The formula for oxalic acid crystals is $C_2H_2O_4, 2H_2O$.

$$\text{Now } C_2H_2O_4, 2\,H_2O = 2 \times 12 + 2 + 4 \times 16 + 2 \times 18 = 126.$$

Also oxalic acid is a dibasic acid and consequently its equivalent is $\frac{126}{2} = 63$. Normal oxalic acid contains therefore 63 gm. $C_2H_2O_4, 2\,H_2O$ per litre.

Weigh out accurately into a 200 c.c. flask about 12·6 gm. (not less) of pure crystallised oxalic acid by means of a weighing bottle. Dissolve up the acid in distilled water and make up to the mark with distilled water.

If exactly 12·6 gm. of the crystals are taken the solution will be accurately normal since one litre (= 200 × 5 c.c.) of it would contain 5 × 12·6 or 63 gm. $C_2H_2O_4, 2\,H_2O$. If the solution is not exactly normal a correction factor may be used, or assuming it is stronger than normal, it may be diluted down till normal.

Suppose, for example, 12·8 gm. of the acid were used. The correction factor would be $\frac{12{\cdot}8}{12{\cdot}6}$ or 1·015. The solution may be made accurately normal as follows:—

200 c.c. of N oxalic acid contain 12·6 gm. $C_2H_2O_4, 2\,H_2O$.

$\therefore 200 \times \frac{12{\cdot}8}{12{\cdot}6}$ or 203 c.c. of N oxalic acid contain 12·8 gm. of $C_2H_2O_4, 2\,H_2O$.

3 c.c. of distilled water must therefore be added to the oxalic acid to make it accurately normal.

N.B.—When a standard solution is made up by simply weighing out an exact quantity of a substance and making up to a known volume, the solution is said to be standardised "synthetically." This can only be done of course when the substance is *known to be pure*. The solutions of sodium carbonate and oxalic acid which you have prepared have been standardised synthetically.

25. Estimation of Caustic Soda and Sodium Carbonate in a sample of Commercial Caustic Soda.—Weigh out about 10 gm. of the sample in a stoppered weighing bottle,

dissolve, and make up to 250 c.c. Shake up well and determine the total alkali in 25 c.c. with the normal oxalic acid you have just prepared. Run in a known volume of oxalic acid so that an excess is present (use about 30 c.c.), boil (to remove CO_2), and titrate the excess of acid with normal caustic soda,* using phenol phthaleïn as indicator (litmus might also be used).

The difference between the total acid run in and the excess of acid determined by titration gives the amount of acid required to neutralise the total alkali and so by calculation the total alkali in 25 c.c. of the solution.

This process of adding a known excess of acid (or alkali) to an alkali (or acid), determining the excess by standard alkali (or acid) and so finding how much alkali (or acid) was neutralised originally, is called "backward titration" or "back titration." In the case under consideration it has the advantage that the CO_2 liberated can all be boiled out before titrating and thus causes no trouble.

Next transfer 25 c.c. of the solution to a 100 c.c. flask, add a little barium chloride solution with shaking till precipitation (of barium carbonate) is complete (probably 2 c.c. will be enough), and make up to the mark with distilled water.

Now shake again so that the liquid is uniformly mixed, withdraw 25 c.c. of the turbid liquid with a pipette, add a few drops of phenol phthaleïn, and run in standard oxalic acid till the pink colour disappears. The volume of acid required measures the amount of caustic soda in the alkaline liquid, the sodium carbonate having been decomposed by the barium chloride according to the equation

$$Na_2CO_3 + BaCl_2 = BaCO_3 + 2\,NaCl.$$

The barium carbonate precipitate does not interfere with the titration as it is not acted upon by oxalic acid.

* This solution if not available must be prepared. Dissolve 20 gm. of pure NaOH in distilled water, and make up to 500 c.c. when cold. Standardise by means of your N oxalic acid, using phenol phthaleïn as indicator.

The total alkali and caustic soda having been determined, the sodium carbonate is found by difference. An example will make clear the method of calculation :—

(1) *Determination of the total alkali.*

Wt. of weighing bottle + caustic soda (1)	= 21·16 gm.
„ „ „ „ „ „ (2)	= 10·91 „
Wt. of caustic soda taken	= 10·25 gm.

This weight of caustic soda was made up to 250 c.c. and 25 c.c. were measured out, 30 c.c.* of N oxalic acid added from a burette, and the excess titrated with N caustic soda.

1*st titration.*—Height of burette (1)	= 1·6 c.c.
„ „ (2)	= 12·3 c.c.
Vol. of N caustic soda	= 10·7 c.c.
2*nd titration.*—Height of burette (1)	= 12·3 c.c.
„ „ (2)	= 22·9 c.c.
Vol. of N caustic soda	= 10·6 c.c.
3*rd titration.*—Height of burette (1)	= 22·9 c.c.
„ „ (2)	= 33·55 c.c.
Vol. of N caustic soda	= 10·65 c.c.

The mean of the three determinations is 10·65 c.c.

Now the volume of N oxalic acid neutralised by this volume of alkali is 10·65 c.c.

∴ The volume of N oxalic acid equivalent to the total alkali in 25 c.c. of the solution of the commercial caustic soda is 30 − 10·65 or 19·35 c.c.

This volume is also equivalent to 19·35 c.c. of N caustic soda which contains $\frac{19{\cdot}35}{1000} \times 40$, or 0·774 gm. NaOH.

* It is not of course necessary to use exactly 30 c.c., but if this is done each time the calculation is simplified.

∴ The total alkali in 25 c.c. of the solution of the commercial product (reckoned in terms of its NaOH equivalent, some of it being actually present as Na_2CO_3) is 0·774 gm.

The percentage of total alkali in the commercial sample (reckoned as NaOH) is therefore

$$\frac{0{\cdot}774}{10{\cdot}25} \times \frac{250}{25} \times 100, \text{ or } \mathbf{75{\cdot}5} \text{ per cent.}$$

(2) *Determination of NaOH.*

25 c.c. of the solution were introduced into a 100 c.c. flask and the Na_2CO_3 precipitated by $BaCl_2$. The turbid liquid was titrated with N oxalic acid.

1*st titration.*—Height of burette	(1) =	3·5 c.c.
„ „	(2) =	20·6 c.c.
Vol. of N oxalic acid	=	17·1 c.c.
2*nd titration.*—Height of burette	(1) =	4·8 c.c.
„ „	(2) =	21·9 c.c.
Vol. of N oxalic acid	=	17·1 c.c.
3*rd titration.*—Height of burette	(1) =	7·45 c.c.
„ „	(2) =	24·6 c.c.
Vol. of N oxalic acid	=	17·15 c.c.

The mean of these results is 17·1 c.c. (within the limits of experimental error).

Now this volume of N oxalic acid is equivalent to 17·1 c.c. of N caustic soda, *i.e.* to

$$\frac{17{\cdot}1 \times 40}{1000} \text{ or } 0{\cdot}684 \text{ gm. NaOH.}$$

This then is the weight of NaOH in the 25 c.c. of solution.

∴ The percentage of NaOH in the commercial sample is

$$\frac{0{\cdot}684}{10{\cdot}25} \times \frac{250}{25} \times 100, \text{ or } \mathbf{66{\cdot}7} \text{ per cent.}$$

Percentage of Na_2CO_3 in the sample.

The difference between the volume of N oxalic acid required to neutralise 25 c.c. of the sample solution before and after the addition of $BaCl_2$ gives the volume required to neutralise the Na_2CO_3 present. This is 19·35 − 17·1 or 2·25 c.c.

Now 2·25 c.c. N oxalic acid neutralise 2·25 c.c. of N sodium carbonate.

Normal Na_2CO_3 contains *half* its *formula weight* (*i.e.* the weight of it represented by its formula) per litre, since it contains two atoms of sodium which are equivalent to two atoms of hydrogen; *i.e.* it contains $\frac{106}{2}$ or 53 gm. Na_2CO_3 per litre.

Therefore the weight of Na_2CO_3 in 25 c.c. of the sample solution is

$$\frac{2{\cdot}25}{1000} \times 53 \text{ gm.}$$

The percentage of Na_2CO_3 in the sample is therefore

$$\frac{2{\cdot}25}{1000} \times 53 \times \frac{250}{25} \times 100 \div 10{\cdot}25, \text{ or } \mathbf{11{\cdot}6} \text{ per cent.}$$

II. Use of Potassium Permanganate.

26. Suppose we are given a solution of ferrous sulphate and asked to determine the strength of it. We know that suitable oxidising agents will convert the ferrous salt into ferric sulphate. If, therefore, a standard solution of such an oxidising agent is prepared we can determine by titration how much of it is required to oxidise a known volume of the ferrous sulphate solution, assuming that a suitable indicator can be found to show when the reaction is complete.

Then from the amount of the oxidising agent used the amount of ferrous sulphate oxidised can be calculated, assuming that the equation expressing the reaction which takes place is known.

Such an oxidising agent is potassium permanganate ($KMnO_4$) in the presence of dilute sulphuric acid, which

acts as its own indicator, since it possesses a very pronounced colour (pink in very dilute solution), whilst when the permanganate is reduced completely (it is now in the form of manganous sulphate, $MnSO_4$) the solution becomes practically colourless.

27. Standard Potassium Permanganate.—Potassium permanganate, $KMnO_4$, may be considered as made up of the two oxides, K_2O and Mn_2O_7 ($K_2O + Mn_2O_7 = K_2Mn_2O_8 = 2\ KMnO_4$), and $MnSO_4$ of MnO and SO_3. We may therefore represent the reduction of potassium permanganate to manganese sulphate by reference to the corresponding oxides of manganese, thus—

$$Mn_2O_7 \rightarrow 2\ MnO + 5\ O.$$

But Mn_2O_7 corresponds to two molecules of $KMnO_4$, and therefore *two molecules of $KMnO_4$ yield five atoms of oxygen available for oxidising purposes*, i.e. of so-called "available" oxygen.

But 5 atoms of oxygen are equivalent to 10 atoms of hydrogen, from which it follows that 2 molecules of $KMnO_4$ are equivalent to 10 atoms of hydrogen. The *equivalent weight* (see § 14) of potassium permanganate, *i.e.* the weight equivalent to 1 atom of hydrogen, is therefore $\frac{1}{10}$ of twice the molecular weight, *i.e.*

$$\frac{2\,(39 + 55 + 4 \times 16)}{10} = \frac{316}{10} = 31{\cdot}6 \text{ gm.}$$

A normal solution of potassium permanganate would then contain 31·6 gm. of $KMnO_4$ per litre, and a decinormal solution 3·16 gm. Also the amounts of available oxygen in a litre of the normal and decinormal solutions respectively are evidently 8 gm. and 0·8 gm., since these weights are equivalent to 1 gm. and 0·1 gm. of hydrogen.

28. Preparation of the Standard Solution.—Weigh out about 3·2 gm. of crystallised $KMnO_4$ and dissolve in one litre of water. Boil the solution in a large basin for a quarter of an hour to fully oxidise any organic matter that may be present, and, when cool, transfer it to a

stoppered bottle. The solution will be approximately decinormal.

(1) *Standardisation by means of iron.* The exact strength of the solution may be determined by making use of the reaction referred to in § 26, namely, the oxidation of ferrous sulphate to ferric sulphate. The equation expressing the reaction which takes place can be built up as follows:—We have seen that two molecules of $KMnO_4$ contain five available atoms of oxygen. Now the oxides corresponding to ferrous and ferric sulphates are FeO and Fe_2O_3 respectively. But

$$10\ FeO + 5\ O = 5\ Fe_2O_3,$$

i.e. five atoms of oxygen will convert *ten* atoms of iron from the ferrous to the ferric state. It follows that two molecules of $KMnO_4$ will oxidise 10 molecules of $FeSO_4$ to $Fe_2(SO_4)_3$, and the equation for the reaction is

$$2KMnO_4 + 10\ FeSO_4 + 8\ H_2SO_4 = 2\ MnSO_4 + K_2SO_4 + 5\ Fe_2(SO_4)_3 + 8\ H_2O.$$

Since a normal solution of $KMnO_4$ contains $\frac{1}{10}$ of twice a gram molecular weight,* one litre of normal $KMnO_4$ will oxidise $\frac{1}{10} \times 10 = 1$ gram atom † of Fe = 56 gm. Fe.

We can, of course, get at this another way, for since 2 FeO require 1 atom of oxygen for conversion into Fe_2O_3, it follows that 2 atoms of Fe are equivalent to 1 atom of oxygen, *i.e.* to 2 atoms of hydrogen. The volume of $KMnO_4$ solution which is equivalent to 1 gram atom of hydrogen (*i.e.* 1 litre of a normal solution) is therefore also equivalent to 1 gram atom of Fe.

Weigh out carefully about 1 gm. of *clean* iron wire ‡ (polish with emery paper if necessary). Fit a round-bottomed flask of about 250 c.c. capacity with a cork carrying a short glass tube, on to which is fitted about an

* A *gram molecular weight* of a substance is the molecular weight of the substance in grams.

† A *gram atom* of an element is the atomic weight of the element in grams.

‡ The iron wire should be the purest obtainable. Pianoforte wire is very suitable; it contains about 99½ per cent. of iron.

inch of rubber tubing with a vertical slit cut in the centre as shown in Fig. 25. The open end of the rubber tube is closed by a bit of glass rod. This arrangement is known as a "Bunsen valve." When the pressure on the inside, *i.e.* the concave side, of the valve is increased the sides of the slit open and gas escapes, but when the pressure on the outside, *i.e.* the convex side, increases the sides of the slit are forced together and air cannot enter.

Fig. 25.

Pour about 70 c.c. of dilute sulphuric acid into the flask, then add about 1 gm. of sodium carbonate and finally the weighed iron wire. Introduce the cork and Bunsen valve. Heat the flask gently until the wire is dissolved and then allow the flask to cool. The carbon dioxide generated by the action of the acid on the sodium carbonate displaces the air from the flask, and, as explained above, air cannot enter through the valve during the cooling, so that oxidation of the ferrous sulphate solution is prevented.

In the meantime prepare some air-free water by boiling distilled water in a flask and cooling it rapidly under the tap. Pour the ferrous sulphate solution into a 250 c.c. graduated flask when it is quite cold and wash out the flask several times with the air-free water, which should also be quite cold, transferring the washings to the graduated flask. Make up to the mark with the air-free water and shake up well.

Bring 25 c.c. of the solution into a beaker by means of a pipette, and add about 25 c.c. of air-free water. Run in the permanganate solution from a burette * until the last drop gives a permanganate pink tinge. Repeat three or four times and take the mean of the results. In calculating the strength of the $KMnO_4$ solution, deduct a half per cent. from the weight of the wire taken, for impurities. Label the bottle according to the amount of iron which

* A burette with a *glass stopcock* must be used. Some burettes terminate in a glass jet attached by a piece of rubber on which is a metal clip. Such a burette is inadmissible when permanganate is used, since the rubber would undergo oxidation.

1 c.c. of the solution will oxidise, or according to the amount of $KMnO_4$ which 1 c.c. of the solution contains. For example, if it is exactly decinormal, we shall have 1 c.c. = ·0056 gm. Fe (for 1 litre = 1000 c.c. = $\frac{56}{10}$ gm. Fe), or 1 c.c. = ·00316 gm. $KMnO_4$ (since 2 $KMnO_4$ = 316 and therefore 1 litre or 1000 c.c. = $\frac{316}{10 \times 10}$ gm. $KMnO_4$).

Suppose that in an experiment the following results were obtained :—

Wt. of iron taken = 0·972 gm.

Volume of permanganate used in titrating 25 c.c. of the iron solution (average of three titrations) = 17·1 c.c.

Now 250 c.c. of the iron solution contains

$$0{\cdot}972 - \tfrac{1}{200} \times 0{\cdot}972 \text{ or } 0{\cdot}967 \text{ gm. Fe}$$

(deducting ½ per cent. for impurities).

∴ 25 c.c. contains 0·0967 gm. of iron.

This volume reduces 17·1 c.c. of the $KMnO_4$ solution.

∴ 1 c.c. of the $KMnO_4$ solution is equivalent to

$$0{\cdot}0967 \div 17{\cdot}1 \text{ or } \mathbf{0{\cdot}00566} \text{ gm. Fe.}$$

Or since 56 gm. of iron are equivalent to 31·6 gm. of $KMnO_4$,

1 c.c. of the $KMnO_4$ solution contains

$$0{\cdot}00566 \times \frac{31{\cdot}6}{56} \text{ or } \mathbf{{\cdot}00319} \text{ gm. } KMnO_4.$$

The amount of water which must be added to the solution in order to make it accurately decinormal is readily calculated.

1 litre of the $KMnO_4$ solution contains

$$1000 \times {\cdot}00319 \text{ or } 31{\cdot}9 \text{ gm. } KMnO_4.$$

Now 1 litre of $\frac{N}{10}$ $KMnO_4$ contains 31·6 gm. $KMnO_4$.

∴ The volume of $\frac{N}{10}$ potassium permanganate which contains 31·9 gm. $KMnO_4$ is $\frac{31{\cdot}9}{31{\cdot}6} \times 1000$ or 1010 c.c.

∴ In order to make the permanganate solution accurately decinormal 10 c.c. of water must be added and the liquid well shaken to make the composition uniform.

(2) *Standardisation by means of oxalic acid.* Oxalic acid is really oxidised completely to carbon dioxide and water by a hot solution of potassium permanganate in the presence of dilute sulphuric acid.

The essential change is represented by the equation

$$H_2C_2O_4, 2\,H_2O + O = 2\,CO_2 + 3\,H_2O,$$

i.e. one molecule of oxalic acid is oxidised by one atom of oxygen, which is equivalent to two atoms of hydrogen. A normal solution of oxalic acid will therefore contain $\frac{126}{2}$ or 63 gm. per litre (since $H_2C_2O_4, 2\,H_2O = 126$).

The equation representing the reaction which takes place when oxalic acid is oxidised by potassium permanganate in the presence of dilute sulphuric acid is

$$\underset{630}{5\,H_2C_2O_4, 2\,H_2O} + \underset{316}{2\,KMnO_4} + 3\,H_2SO_4 = 10\,CO_2 + K_2SO_4 + 2\,MnSO_4 + 18\,H_2O.$$

Now we have seen that a normal solution of potassium permanganate contains 31·6 gm. per litre. The normal solutions of oxalic acid and potassium permanganate must be of equivalent strength, so that if the equation given above is correct the weights of oxalic acid and potassium permanganate must be in the ratio 63 : 31·6. This is the case, for 630 : 316 = 63 : 31·6.

Weigh out accurately about 1·6 gm. of pure crystallised oxalic acid, dissolve in water, and make up to 250 c.c. The solution will be about decinormal. Measure out 25 c.c. of it into a beaker, add about an equal volume of dilute sulphuric acid, heat the liquid to about 60°C. (*i.e.* till the beaker is too hot to touch except momentarily), and run in the permanganate solution till the last drop just turns the liquid permanently pink. Repeat the titration twice and take the mean of the results.

The permanganate solution must not be run in too rapidly or a brown precipitate forms which is not got rid

of easily. In any case the oxidation does not take place so rapidly as in the case of ferrous sulphate, and each time the permanganate is run in a brown coloration is formed which gradually disappears. As the end of the reaction is approached it is therefore important to add the permanganate very gradually, in order that the exact point when the solution acquires a permanent pink tinge may be determined.

Suppose that in an experiment 1·58 gm. of oxalic acid were made up to 250 c.c., and that as a mean of three titrations 24·9 c.c. of the permanganate solution were required to oxidise 25 c.c. of the oxalic acid solution.

Now 25 c.c. of the oxalic acid solution contain

$$\frac{25 \times 1{\cdot}58}{250} \text{ or } 0{\cdot}158 \text{ gm. } H_2C_2O_4, 2\,H_2O.$$

This is equivalent to $0{\cdot}158 \times \frac{31{\cdot}6}{63}$ gm. of $KMnO_4$.

∴ 1 c.c. of the permanganate solution contains

$$0{\cdot}158 \times \frac{31{\cdot}6}{63} \times \frac{1}{24{\cdot}9} \text{ or } {\cdot}00318 \text{ gm. } KMnO_4.$$

29. Precautions to be observed in Titrations with Permanganate:—

(1) A sufficient excess of sulphuric acid must always be present to prevent the separation of a precipitate of oxide of manganese. If the solution becomes brown or turbid, add more sulphuric acid till clear.

(2) Hydrochloric and nitric acids must be avoided during the titration, as these acids complicate the reaction with permanganate and are a source of error. In the case of hydrochloric acid there is a tendency for the permanganate to oxidise the acid with liberation of chlorine.

(3) Freshly boiled water, free from dissolved oxygen, should be used, and during titration undue contact with air (by shaking, etc.) should be avoided, as ferrous salts and like compounds are usually subject to oxidation under the action of air.

This precaution does not apply in the case of oxalic acid.

30. Determination of the percentage of Iron in a Ferrous Salt.—Ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2,6H_2O$, is a convenient salt to use. Weigh out accurately about 5 gm. of the pure salt, which you prepared for an earlier experiment, dissolve it in air-free water containing a little sulphuric acid (which prevents the formation of a basic salt), and make up the solution when cold to 250 c.c. Measure out 50 c.c. of this solution, add about 25 c.c. of dilute sulphuric acid, and titrate with decinormal potassium permanganate. Repeat the titration two or three times, and take the mean of the results.

Suppose that in an actual experiment 5·17 gm. of the ferrous ammonium sulphate were weighed out and that the average volume of $\frac{N}{10}$ permanganate used was 26·2 c.c.

The whole 250 c.c. of iron solution would require

$$26{\cdot}2 \times 5 \text{ or } 131 \text{ c.c. of } \frac{N}{10}\ KMnO_4.$$

Now 1 c.c. $\frac{N}{10}\ KMnO_4$ is equivalent to ·0056 gm. of Fe.

$\therefore$ 131 c.c. $\frac{N}{10}\ KMnO_4$ are equivalent to $131 \times {\cdot}0056$ gm. of Fe,

i.e. the percentage of Fe in ferrous ammonium sulphate is

$$\frac{131 \times {\cdot}0056}{5{\cdot}17} \times 100, \text{ or } \mathbf{14{\cdot}2} \text{ per cent.}$$

The calculated percentage is **14·3**.

Compare your result with that you obtained by the gravimetric method, § 6.

Pure ferrous ammonium sulphate may be used instead of (or as a check on) iron wire or oxalic acid for standardising potassium permanganate, but great care must be exercised in the selection of the crystals used; they should show no trace of a brown colour (produced by oxidation).

31. Determination of the percentage of Iron in a Ferric Salt.—In order to determine the iron in a ferric salt by

means of potassium permanganate the iron must first be reduced to the ferrous state. This is conveniently brought about by the action of zinc and dilute sulphuric acid.

Weigh out accurately about 12 gm. of recrystallised ammonium iron alum, $(NH_4)_2SO_4, Fe_2(SO_4)_3, 24\,H_2O$, into a graduated 250 c.c. flask, dissolve in water, add a little dilute sulphuric acid, and make up to the mark.

Measure out 100 c.c. of this solution into a small flask, add a few c.c. of concentrated sulphuric acid, and then some fragments of zinc *free from iron.** Close the flask with a cork fitted with a Bunsen valve (Fig. 25).

The nascent hydrogen set free by the action of the sulphuric acid on the zinc reduces the ferric sulphate to ferrous sulphate according to the equation

$$Fe_2(SO_4)_3 + \underset{\text{nascent}}{2\,H} = 2\,FeSO_4 + H_2SO_4.$$

The solution of the zinc should be assisted towards the finish by gently warming the flask. It is essential for the zinc to be *completely dissolved* before the titration is made; otherwise the nascent hydrogen which is being produced would reduce some of the permanganate. If necessary more acid must be added in order to complete the solution.

In order to test whether the reduction of the iron is complete place a drop of ammonium thiocyanate on a white tile. Now take out a drop of the liquid in the flask on the end of a glass rod and add it to the thiocyanate. If a red coloration is produced (due to the formation of *ferric* thiocyanate) the reduction is not complete. In this case more zinc must be introduced, and when it has completely dissolved the test must be repeated.

When the reduction is complete cool the flask under the tap, transfer the solution to a 250 c.c. flask, washing out several times with air-free water, make up to the mark, and then titrate 50 c.c. of the solution with decinormal permanganate. Repeat the titration two or three times.

* Otherwise $FeSO_4$ would be formed, and this would, of course, introduce an error.

Suppose that in an experiment 11·76 gm. of the iron alum were weighed out and titrated as above and that the average volume of $\frac{N}{10}$ $KMnO_4$ required for the titration of 50 c.c. of the reduced iron solution was 19·5 c.c. The volume of $\frac{N}{10}$ $KMnO_4$ required for the whole 250 c.c. would be 19·5 × 5, or 97·5 c.c.

Now 97·5 c.c. of $\frac{N}{10}$ $KMnO_4$ are equivalent to 97·5 × ·0056 gm. of iron.

This then is the weight of iron in 100 c.c. of the original iron solution, and the weight in the whole 250 c.c. is

$$97{\cdot}5 \times {\cdot}0056 \times \tfrac{250}{100} \text{ gm.}$$

Therefore the percentage of iron in ammonium iron alum is $\frac{97{\cdot}5 \times {\cdot}0056 \times 2{\cdot}5 \times 100}{11{\cdot}76}$ or **11·6** per cent.

Now $(NH_4)_2, Fe_2(SO_4)_3, 24\ H_2O$
$= 2 \times 18 + 2 \times 56 + 4 \times 96 + 24 \times 18$, or 964

The theoretical percentage of iron is therefore
$\frac{112}{964} \times 100$, or **11·6** per cent.

32. Determination of the amount of Ferrous and Ferric Iron in 1 litre of a solution containing both.—25 c.c. (say) of the solution are titrated with standard potassium permanganate. This gives the iron present in the *ferrous* state. 100 c.c. of the solution is reduced with zinc and dilute sulphuric acid, the liquid made up to 250 c.c., and portions of 50 c.c. then titrated with the standard permanganate; this gives the *total* iron. The iron present in the *ferric* state is formed by difference.

Example.—25 c.c. of the given solution required 16 c.c. of a solution of $KMnO_4$ labelled "1 c.c. = ·00545 gm. Fe."
25 c.c. of the iron solution contain therefore 16 × ·00545 gm. of iron in the ferrous state,

i.e. 1 litre of the solution contains $\frac{1000}{25} \times 16 \times \cdot00545$ gm. or **3·49** gm. of ferrous Fe.

Further, 50 c.c. of the solution obtained after reduction with zinc and sulphuric acid and dilution as above required 24·5 of the standard permanganate (mean of 3 titrations).

The total iron in 50 c.c. of the reduced solution is therefore $24{\cdot}5 \times {\cdot}00545$ gm.

∴ Total iron in the 250 c.c. of reduced solution is $24{\cdot}5 \times {\cdot}00545 \times 5$ gm.

This is the total amount of iron contained in 100 c.c. of the original solution, and the amount in a litre is therefore $24{\cdot}5 \times {\cdot}00545 \times 5 \times 10$, or **6·68** gm.

The amount of *ferric* iron in **1** litre of the solution is by difference 6·68 — 3·49, or **3·27** gm.

In order to carry out the above estimation make up a solution containing known amounts of ferrous ammonium sulphate and ammonium iron alum by weighing out, say, 3 gm. of the former salt and 5 gm. of the latter and making up to 250 c.c. with air-free water. Proceed as above and compare your results with the theoretical percentages of ferrous and ferric iron, calculated from the weights of the salts taken.

33. Estimation of the percentage of the Acid Radicle (C_2O_4) in a Soluble Oxalate.—This is readily carried out by means of standard permanganate. A known amount of the salt is treated with excess of dilute sulphuric acid and the oxalic acid liberated is determined by titration with standard $KMnO_4$.

Weigh out accurately about 1·5 gm. of pure *salts of lemon*,* KHC_2O_4, $H_2C_2O_4$, $2\,H_2O$, dissolve in water and make up to 250 c.c. Measure out 25 c.c. of the solution into a beaker, add an equal volume of dilute sulphuric acid and titrate with standard $KMnO_4$ $\left(\text{about } \frac{N}{10}\right)$.

Suppose that in an experiment 1·48 gm. of salts of lemon was made up to 250 c.c. and that 25 c.c. of the

* Also called *salts of sorrel*.

solution required (as a mean of several titrations) 23·1 c.c. of $\frac{N}{10}$ $KMnO_4$.

The 250 c.c. would require 231 c.c. of $\frac{N}{10}$ $KMnO_4$, which would oxidise 231 c.c. of $\frac{N}{10}$ oxalic acid.

But we have already seen (§ 28) that normal oxalic acid contains half its gram molecular weight per litre; therefore it will contain half the weight of the acid radicle (C_2O_4) in grams per litre, *i.e.* $\frac{1}{2} \times (24 + 64)$, or 44 gm. per litre.

$\therefore$ 231 c.c. of $\frac{N}{10}$ oxalic acid will contain

$$\frac{231}{1000} \times \frac{1}{10} \times 44 \text{ gm. of } (C_2O_4),$$

i.e. the percentage of (C_2O_4) in salts of lemon is

$$\frac{231}{1000} \times \frac{1}{10} \times 44 \times \frac{1}{1{\cdot}48} \times 100, \text{ or } \mathbf{68{\cdot}7} \text{ per cent.}$$

The calculated percentage is **68·3**.

III. Use of Silver Nitrate.

34. Estimation of Chlorine in a Neutral Solution of a Chloride by means of Standard Silver Nitrate.—A standard solution of silver nitrate is prepared and run into a measured volume of the chloride solution till precipitation of silver chloride is complete. The exact point at which this occurs can, however, only be ascertained by a tedious and prolonged process unless a third substance is used as indicator. The substance used for this purpose is potassium chromate (K_2CrO_4), a few drops of which are added to the chloride solution before the silver nitrate is run in. As long as any chloride remains in solution the silver nitrate reacts with it and not with the potassium chromate; but as soon as the precipitation of silver chloride is complete the further addition of a drop of silver nitrate produces a precipitate of red silver chromate

(Ag_2CrO_4). The appearance of a faint reddish colour therefore marks the close of the reaction.

Precautions to be observed.—(1) Since silver chromate is soluble in acids the titration can only be conducted in *neutral* solution. If therefore the solution is acid it must be just neutralised with sodium carbonate before titration. Also if the solution of potassium chromate is found to have an acid reaction it should be just neutralised with sodium carbonate.

(2) Only sufficient potassium chromate must be added to give a *very faint* yellow tinge to the liquid.

(3) The titration must be carried out *in the cold.*

35. Preparation of Decinormal Silver Nitrate Solution—Since one molecule of silver nitrate ($AgNO_3$) contains one atom of silver which is equivalent to one atom of chlorine, a decinormal solution of silver nitrate will contain $\frac{1}{10}$th of a gram molecule of $AgNO_3$ per litre, *i.e.* $\frac{1}{10} \times (108 + 14 + 48)$ or 17 gm. per litre.

Weigh out accurately about 4·25 gm. (not less) of pure $AgNO_3$, dissolve in cold water, and make up to 250 c.c. Make the solution accurately decinormal by suitably diluting it in the usual way, or simply label it the exact strength (most conveniently in terms of chlorine) as calculated from the weight of salt dissolved.

For example, suppose 4·28 gm. $AgNO_3$ were weighed out. Then 1 c.c. of the solution contains $\frac{4 \cdot 28}{250}$ or 0·0171 gm. $AgNO_3$, which is equivalent to $\frac{35 \cdot 5}{170} \times \cdot 0171$, or ·00357 gm. of chlorine.

The solution would therefore be labelled

1 c.c. = ·00357 gm. chlorine.

36. Estimation of the percentage of Chlorine in Sodium Chloride.—Weigh out accurately about 1·5 gm. of pure sodium chloride, dissolve in cold water, and make up to

250 c.c. Measure out 25 c.c. of the solution into a beaker, add about an equal volume of water, and then two or three drops of potassium chromate solution. Now run in the standard silver nitrate solution gradually with stirring till the liquid just acquires a permanent reddish tinge. Repeat the titration as usual.

Suppose that the weight of sodium chloride taken was 1·48 gm. and that 25 c.c. of the chloride solution required, as a mean of three titrations, 24·9 c.c. of standard silver nitrate, 1 c.c. of which = ·00357 gm. chlorine.

The weight of chlorine in the 25 c.c. of solution is therefore 24·9 × ·00357 gm., and in the 250 c.c.

$$24{\cdot}9 \times {\cdot}00357 \times 10 \text{ gm.}$$

∴ The percentage of chlorine in sodium chloride is

$$24{\cdot}9 \times {\cdot}00357 \times 10 \times \frac{100}{1{\cdot}48}, \text{ or } \mathbf{60{\cdot}1} \text{ per cent.}$$

The theoretical percentage is **60·7**.

37. Determination of Silver in Neutral Solution by means of standard Sodium Chloride.—This process is similar to the preceding. A decinormal (about) solution of sodium chloride (= 5·85 gm. NaCl per litre, since NaCl = 23 + 35·5, or 58·5) is prepared by dissolving about 1·46 gm. (not less) of NaCl in 250 c.c. of water. The solution is made exactly decinormal by suitable dilution, or instead the exact strength calculated from the weight of salt dissolved may be stated on the containing vessel.

The titration cannot be satisfactorily carried out by measuring out a known volume of the silver nitrate solution, adding potassium chromate, and running in standard sodium chloride solution. Instead it is performed as in the preceding determination, 25 c.c. of the sodium chloride solution being measured out into a beaker and titrated with silver nitrate solution.

PART III.

QUALITATIVE ANALYSIS.

Qualitative Analysis has for its object the determination of the number and nature of the constituents of substances without reference to their proportions.

Usually it has reference to the examination of *salts*, *i.e.* combinations of *acids* and *bases*, and in such cases the problem involved is the determination of the particular base and acid present in any given substance. Thus we examine substances to determine, not directly what *elements* are present, but what metals and what acid radicles—the latter, of course, being usually groups of elements.

In determining the metal or metals present in a given substance we submit a portion of the substance to the action of various reagents. These reagents are applied in the dry way, *e.g.* before the blowpipe, or in the wet way, *i.e.* in the state of solution. The latter method is the more important. Usually, the phenomenon which we take advantage of in detecting any substance is the formation of a *precipitate*, when solutions of certain bodies are brought together. The formation of a precipitate, of course, is due to the interaction of the substances in solution giving rise to the production of some new compound which is insoluble, or only slightly soluble, in water.

Reagents are divided into *Group reagents* and *special reagents*. The former are those which produce a similar general result with several metals—*e.g.* Hydrochloric acid

gives a white precipitate with either silver, mercury, or lead, and is therefore the group reagent for those metals.

Special reagents are those which we make use of for confirming the presence or absence of a certain metal. In applying reagents to a body to be analysed, it is of the utmost importance that they should be used in a systematic order; otherwise altogether erroneous results may be obtained.

The group reagents usually employed are the following:— Hydrochloric acid; Sulphuretted hydrogen in presence of hydrochloric acid; Ammonia in presence of ammonium chloride; Ammonium sulphide in presence of ammonia and ammonium chloride; Ammonium carbonate in presence of ammonia and ammonium chloride, applied in the above order.

The metals are usually divided into six* groups, according to their behaviour with the above reagents.

Group I. comprises those metals whose chlorides are insoluble in water, and which, therefore, are precipitated by hydrochloric acid (or, indeed, by any soluble chloride). They are Silver, Lead, and Mercury (ous).

Group II. comprises *those of the remaining metals* whose sulphides are insoluble in hydrochloric acid, and which, therefore, are precipitated by sulphuretted hydrogen in presence of that acid. They are Mercury (ic), Lead Bismuth, Copper, Cadmium, Tin, Antimony, and Arsenic.

Group III. includes *those of the remaining metals* whose hydroxides are insoluble in water and in ammonium chloride solution, and which, therefore, are precipitated by ammonia in presence of ammonium chloride. They are Iron, Chromium, and Aluminium.

Group IV. consists of *those of the remaining metals* whose sulphides are insoluble in water, and which, therefore, are precipitated by ammonium sulphide in alkaline solutions. They are Nickel, Cobalt, Manganese, and Zinc.

Group V. includes, of *the remaining metals*, those whose carbonates are insoluble in water and ammonium salts,

* These divisions and the group reagents must be perfectly familiarised before commencing systematic analysis.

and which, therefore, are thrown down by ammonium carbonate in presence of ammonium chloride. They are Barium, Strontium, and Calcium.

Group VI. comprises *the remaining metals*, for which there is no general reagent. They are Magnesium, Potassium, Sodium, and Ammonium.

Special notice should be taken of the words "of the remaining metals" which appear so often in the above account. Group IV., for example, does not consist of all the metals which are precipitated by ammonium sulphide in alkaline solutions, but only of those remaining after the removal of Groups I., II., and III., which are thus precipitated.

After determining the group to which a metal belongs, the next thing is to find which of the several metals in that group it is. Advantage is taken of the slight differences in the properties of the similar compounds of different metals existing in the same group—*e.g.* as to colour, solubility in various reagents, etc.—in order to settle this question; and, finally, the answer is confirmed and substantiated by the application of a *special* or *confirmatory* test. In testing for the acid radicles the splitting up of the various acids into groups cannot be so fully carried out, and more importance is to be attached to confirmatory or special reactions.

It must carefully be borne in mind that analysis is founded upon a knowledge of the properties of the metals and acids, and is really an application of such chemical knowledge to the question in hand. The student should, therefore, in all cases endeavour to understand clearly the chemical changes which are produced in the various operations of chemical analysis. To this end he will derive great advantage by making it a rule to express by means of equations the various reactions which he performs. These equations should be written in a note-book at the time the experiments are being made in the laboratory.

It will be found that almost all reactions made use of in analysis are examples of metathesis or double decomposition, *e.g.* the interchange of acids and bases—thus barium chloride and sodium sulphate give us sodium

chloride and barium sulphate; the latter, being insoluble in water, is thrown down as a white precipitate.

$$Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl.$$

Such reactions, of course, present little difficulty, but the practice of writing the equations should be adhered to, even in simple cases, as by this means the student acquires a valuable familiarity with the valency of metals and the basicity of acids.

Rules for Qualitative Analysis:—

(1) **Use small quantities** of the substance to be tested, even if you have a large stock of it at your disposal; otherwise reactions will often be masked, especially those performed in the dry way. If you have only a small allowance, treasure it, and always keep some in reserve to fall back upon.

(2) **Work systematically**, avoid making random shots, and **record your processes and results** in an orderly way.

(3) **Do not assume** what you think **ought** to have happened if it does not; the basis of your expectation may be erroneous, and in laboratory practice should be confirmed, though it is foolish to follow up an unsatisfactory result in an examination.

(4) **Make a note of seeming discrepancies** of results: you will probably find the explanation later yourself.

(5) **Keep your test-tubes and vessels scrupulously clean.** Wash them and your platinum wire at the end of your work each day; try the wire alone in the flame before using it.

(6) **Be exact in carrying out the directions given**

CHAPTER I.

INTRODUCTORY EXPERIMENTS.

To bend a piece of glass tubing.—Take a piece of $\frac{3}{16}$-inch soft tubing, and hold it horizontally in the upper part of an ordinary luminous gas flame, with its length in the plane of the flame. Turn the tubing slowly round and round so as to heat it uniformly. When it begins to soften, remove it from the flame and bend it slowly and carefully to the required shape. Allow to cool, and *then* remove the coating of soot from the bend.

To cut narrow glass tubing with a file.—Take a piece of glass tubing and lay it on a table. Taking hold of it with the finger and thumb of the left hand near the point where it is to be cut, draw one edge of a sharp triangular file *once* across it, from heel to point. The tube can now be broken by forcibly attempting to bend it away from the file scratch, and at the same time trying to pull it apart. The cut ends must then have their sharp edges rounded by holding the tube vertically in the Bunsen flame, until the flame is coloured strongly yellow by the sodium of the glass.

To draw out a piece of glass tubing; to make a jet.—Take a short piece of tubing and heat the middle portion in a small blow-pipe flame, supporting each end of the tube with the fingers, and continually turning it round so as to equally heat all sides; when the tube is quite soft, remove it from the flame and slowly draw it out. The more slowly it is drawn out, the more gradually will the tube taper

towards the centre. Then with a file cut the tube at a suitable point, round off the cut ends in the flame, and the jet is ready for use.

To make a Bulb-tube.—Take a piece of $\frac{3}{16}$-inch tubing about 6 inches long, and heat one end in the blowpipe flame until it is completely closed and rounded off. Before this rounded end becomes too thick, take it out of the flame, and holding the tube vertical blow into it steadily, but not too strongly, until a small bulb is blown at the heated end.

Use of Spatula.—It is often necessary to take a small quantity of some solid substance out of a bottle. For this purpose the spatula—an instrument very like a small table knife—is used. A small bone or ivory paper cutter answers the purpose very well. The blade of a penknife is sometimes used, but the use of iron or steel is objectionable. A platinum spatula is the best to use.

To fix a platinum wire in a glass holder.—Take 6 inches of narrow glass tubing and draw it out a little in the middle. Cut in two at the middle of the drawn-out part. Into the narrow cut end insert a piece of platinum wire about 2 inches long; then hold this end in the flame until the glass closes round the wire. A piece of glass rod makes a better holder. Draw the rod out and cut in two as described above. Then hold the narrow end of the rod in the flame until it is quite soft, and insert the piece of platinum wire into the soft end.

The platinum wire thus mounted will be in frequent use for flame tests, and should be kept dipping in hydrochloric acid in a test-tube. This can be done by fitting the holder with a cork which fits into the mouth of the test-tube Kept in this way the wire is always clean.

Flame tests.—(1) Place a small quantity of solid sodium carbonate, Na_2CO_3, on a watch-glass. Lift a small portion of it with the loop of the platinum wire, and hold in the lower outer part of the Bunsen flame. The flame shows an intense yellow colour, characteristic of sodium compounds.

Clean the wire by holding it in the flame until all trace of the yellow coloration disappears. Then wash it in dilute HCl and again heat it.

(2) Take some baryta (or any barium salt) and heat it in the same way. The flame is of a yellowish-green colour, but possibly not very intense. Pour a few drops of HCl into a watch-glass, dip the loop of the wire in it, and take up with the moistened wire a few particles of the salt. On now placing the wire in the flame, the yellowish-green coloration will be much more intense. Now clean the wire by alternately dipping it in HCl and heating it in the flame. For a time the effect of this is merely to increase the intensity of the coloration, but after some time it becomes fainter, and by using fresh acid once or twice the wire can be thoroughly cleaned. Barium compounds are the most difficult to remove from the wire.

(3) Take some strontium nitrate and treat in the way described above. The flame is coloured an *intense* crimson; moistening with HCl makes the flame more intense. Clean the wire, wash it and put it away in a corked test tube or bottle.

Borax bead reactions.—Fused borax possesses the power of dissolving many metallic oxides and salts with formation of compounds which often possess distinctive colours, and so afford valuable tests.

(1) Take a piece of platinum wire fitted with a glass handle as already described, but without a loop at the end; heat in the Bunsen flame, and dip into powdered borax. Some of the salt will adhere to the wire. Again heat the wire, when the borax upon it will first "intumesce," *i.e.*, swell up from the escape of its water of crystallization, and then fuse quietly to a clear, colourless bead. Now take a small quantity of a manganese compound, *e.g.*, $MnSO_4$ or MnO_2, and bring it into contact with the bead, and again heat in the *outer* part of the Bunsen flame; a characteristic *purple* or *amethyst* colour will be produced. If now the air-holes at the base of the lamp be partially closed, so as to produce a slight luminous appearance in the upper

central portion of the flame, and the bead be heated in this flame ("reducing flame"), since there is an excess of coal-gas there, the oxide of manganese, existing as borate in the bead, will be reduced to a lower state of oxidation, and the bead will, when cooled (best in the coal-gas at the centre of the base of the Bunsen flame), be found to be colourless. Treated in a similar way, Chromium compounds give a *green* bead in either flame; Iron, a *reddish-yellow*, in the oxidizing, *greenish-yellow* in the reducing flame; Cobalt, a *bright blue* in either flame, etc., etc. In all cases only a very small quantity of the substance to be tested must be used, otherwise the colour produced is too dark to be recognizable.

The Blowpipe.—To acquire the proper use of the blowpipe will necessitate a good deal of practice. A *continuous* blast of air must be kept up; for this purpose it is necessary to blow without interfering with the breathing. The secret of doing so is to use the cheeks to blow with, and to breathe through the nose. If the cheeks be blown out, it will be found that the air can be forced out of the mouth by contraction of the cheeks at the same time as inspiration is effected through the nose. By long practice this may be done continuously. When blowing continuously, however, since the air is forced out of the mouth by the pressure of the cheeks—not by their contraction—they must be kept distended. It is not necessary to blow hard: a very gentle blast suffices.

To obtain the blowpipe flame, the air-holes at the bottom of a Bunsen burner are closed so as to give a smoky luminous flame, and the blast of air from the nozzle of the blowpipe is then directed across this flame so as to produce a long straight pointed flame. It is used for observing the effects of a very high temperature on different substances, and in some cases to effect their oxidation or reduction.

To oxidize a substance it is heated in the outer flame—that is, at the tip of the blowpipe flame. To effect reduction, the inner flame must be used—that is, the substance

is heated in the centre of the blowpipe flame, which for this purpose must show a small luminous streak in the centre.

Experiments with the Blowpipe.—(1) Take a piece of hard charcoal and scrape a small groove near one end. In this groove place a small quantity of litharge (lead oxide) and direct on it a reducing flame. In a short time it will melt, and if the heating be continued long enough a globule of lead will remain on the charcoal. This is an example of reduction effected by the reducing-flame and the charcoal.

(2) Take some potassium nitrate, KNO_3, and, having placed it on charcoal as described in (1), bring the blowpipe flame to bear on it. It suddenly flares up, and burns a portion of the charcoal with it. This is *deflagration*.

(3) Take weights of powdered sodium carbonate, Na_2CO_3, and potassium carbonate, K_2CO_3, proportionate to their molecular weights, and mix them thoroughly. This mixture is known as *fusion mixture*, and should be kept ready for use. Take a small quantity of litharge (lead oxide), mix it with three or four times its weight of *fusion mixture*, and heat the mixture on charcoal before the blowpipe. The mass fuses, and in a short time small globules of lead appear and are readily fused into one large globule. The use of the fusion mixture is twofold—it prevents the fused litharge from being absorbed by the charcoal, and the fusion and reduction are more easily effected than in experiment (1). The fusion mixture here acts as a *flux*.

Note.—When a substance is to be *reduced*, it should be heated on *charcoal*, with some suitable flux, in the *reducing flame*. If *oxidation* is to be effected, it should be heated on the platinum wire, or on a piece of platinum foil in the oxidizing flame.

(4) Take some zinc oxide, ZnO, mix it carefully with fusion mixture, and heat on charcoal before the blowpipe. The oxide is reduced to the metallic state,* and zinc, being

* The student is not to suppose that the zinc can be *isolated* in this way; it is far too easily oxidizable and the production of the metal is only a *transition stage*.

volatile, burns on passing through the outer flame with a bluish-green flame, forming the oxide which is deposited on the charcoal in the form of an *incrustation*, which is yellow when hot and white when cold. Now moisten the mass with a few drops of cobaltous nitrate, and again heat in the outer flame. The mass now assumes a fine green colour.

(5) Take a small quantity of tin oxide, and mix it with powdered potassium cyanide, KCN; place the mixture on charcoal, and cover it over with a little KCN, then heat before reducing blowpipe flame. The tin oxide is quickly reduced, and small globules of metallic tin are obtained. Substances that are not easily reduced by charcoal alone are readily reduced in the presence of KCN, owing to the tendency of that compound to take up oxygen or sulphur to form KCNO or KCNS.

(6) Powder some copper sulphate, and mix it with five or six times its weight of fusion mixture. Heat the mixture on charcoal before the inner blowpipe flame. The mass fuses, and the $CuSO_4$ is reduced to metallic copper, which is too infusible to be fused into a globule, and therefore remains on the charcoal as small reddish particles or scales which are not easily detected. Allow the mass to cool, remove it from the charcoal together with the crust of underlying charcoal, and place the whole in a small mortar. Powder it very finely, and transfer the powder to a small beaker. Pour on some water, and stir the whole for some time; on standing, the metallic particles sink quickly, so that if the water be poured off after a short time the copper will be found as a powder at the bottom of the beaker, and may be recognized by the effect of adding a few drops of nitric acid. Iron compounds may be similarly dealt with, and the iron particles are readily detected by means of a magnet.

Sublimation.—(1) Take some ammonium chloride, and place a small quantity in the bulb of a bulb-tube. Holding the stem of the tube with a pair of crucible tongs, heat this substance in the Bunsen flame. It gradu-

ally disappears from the bulb and condenses as a *white sublimate* in the upper part of the tube.

(2) Take some white arsenic, As_4O_6, and heat in a bulb-tube. A glittering white sublimate of As_4O_6 in octahedral crystals is obtained in the upper part of the tube. Mix some As_4O_6 with KCN and powdered charcoal, and heat the mixture in a bulb-tube. A brilliant black metallic mirror of arsenic is obtained in the upper part of the tube.

To make a Wash-Bottle.—Take a 16-oz. flask, either of

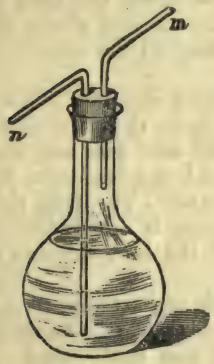

FIG. 26.

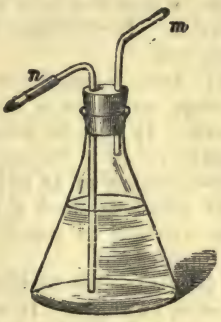

FIG. 27.

the ordinary round form or, better, of the conical shape; fit it with a good cork or indiarubber stopper, in which bore two holes by means of a sharp cork-borer (moistened with glycerine in the case of the rubber cork). Then fit two pieces of tubing bent as shown in Figs. 26 and 27, taking care to round off the ends in the flame, and that the tube *n* ends very close to the bottom of the flask; to the end *n* of the longer tube fit a piece (about $1\frac{1}{2}$ inches) of narrow ($\frac{1}{8}$-inch diam.) indiarubber tubing, carrying at the other end a short piece (about 1 inch) of glass tubing drawn out to a jet. The wash-bottle is to be nearly filled

with distilled water, which can be expelled by blowing down the tube *m*, and the fine stream issuing from the jet can be directed in any desired direction by the flexibility of the rubber tubing. The wash-bottle is used chiefly for washing precipitates on filters and as a reservoir of pure water for general purposes.

To test the solubility of substances.—(1) Take some Epsom salts, $MgSO_4$, $7H_2O$, and with a spatula place a very small quantity of it in a dry test-tube. Half fill the test-tube with water from the wash-bottle, using the jet of water to wash all traces of the salt down the sides of the tube. Close the tube with the thumb, and shake up the solution. It will then be found that all the substance has dissolved.

(2) Take a small quantity of lead chloride, $PbCl_2$, and attempt to make a solution of it in the way described above. It will be found that this salt does not dissolve readily in cold water. Now hold the test-tube in the Bunsen flame so as to boil the water. The lead chloride soon dissolves, and a clear solution is obtained. Allow this solution to stand and cool—the lead chloride again crystallizes out.

(3) Take some barium hydroxide and attempt to make a solution as above. It will be found that this substance is apparently insoluble in both hot and cold water. Take some red litmus paper and test the solution; it will be found to give a strong alkaline reaction, thus showing that a solution has been obtained, and that barium hydrate is slightly soluble in water. Also, place a few drops of the solution on a piece of clean platinum foil and heat over the Bunsen flame. A small white speck is left on the foil showing that the solution contained some solid substance.

(4) Take some pure barium carbonate and treat as above. It will be found insoluble in water (unless, as is frequently the case, it contains traces of the hydroxide). Take a fresh quantity of the substance in a test-tube and pour in some dilute hydrochloric acid, HCl. The carbonate rapidly

dissolves with *effervescence*, carbonic acid gas, CO_2, being evolved.

Precipitation is the basis of testing in the wet way. One of Berthollet's laws of double decomposition may be enunciated thus :—

"Two substances in solution will always decompose each other if it be possible, by double decomposition, to produce another substance less soluble than either of the original substances."

This law expresses the principle of testing by precipitation. For example, take a solution of barium chloride in a test-tube and add to it a small quantity of a solution of magnesium sulphate, $MgSO_4$. The following double decomposition is possible :—

$$BaCl_2 + MgSO_4 = \underset{\text{(soluble)}}{BaSO_4} + MgCl_2.$$

Now barium sulphate, $BaSO_4$, is quite insoluble in water and acids, and therefore the reaction takes place and a white precipitate of $BaSO_4$ is produced.

This reaction now furnishes us with a test for the detection of barium compounds and also for sulphates; for the test is based on the insolubility of $BaSO_4$, and may therefore indicate Ba or H_2SO_4, but has nothing to do with Mg or HCl. A consideration of the reaction given below will further explain this :—

$$Ba(NO_3)_2 + Na_2SO_4 = \underset{\text{(soluble)}}{BaSO_4} + 2\ NaNO_3.$$

Substances employed in systematic analysis for the detection of other substances are called *reagents*.

Solutions of gases or of solids, with other liquids so employed, are called "*wet*" reagents; those used in the solid form, "*dry*" reagents. Solutions used as wet reagents should not be too concentrated.

Filtration.—*To fold a filter paper.*—If, as is usually the case, the precipitate is required as well as the clear liquid,

an ordinary plain filter answers best. In cases where the amount of precipitate is only small, and the filtrate is the portion desired, a ribbed or folded filter should be used, as the liquid flows through such a paper much more quickly than through a plain filter.

To fold a plain filter.—Take a circular piece of filtering paper of the requisite size, and fold it in half. Then again fold it in half, so as to form a quadrant. Now open it in such a way that a cone of paper is formed having one thickness of paper on one side and three thicknesses on the other. Take a plain funnel (*i.e.*, not a fluted one) having an angle of 60° at the apex, and fit the filter paper carefully into it, and moisten the paper with water. The paper should be in contact with the glass in every part, and ought in all cases to be small enough to go entirely into the funnel, and leave a small portion of the glass uncovered all round its upper edge.

If, as sometimes happens, the angle of the funnel is not exactly 60°, it will be found that the paper will not fit accurately to the glass. In this case, fold the filter paper the second time not exactly in half, and open the smaller or larger side according to whether the angle of the funnel is less or greater than 60°.

A little care in folding and fitting the paper to the funnel is well repaid by the greater rapidity with which the liquid will flow through; and, since filtration is the most tedious operation in analytical work, any means by which it can be facilitated is well worth attention.

Certain precipitates—*e.g.*, silver chloride—filter easily and rapidly in the usual way, whilst others—*e.g.*, aluminium or ferric hydroxide—filter very slowly by the ordinary method. In order to increase the rapidity of filtration in such cases, the following arrangement may be used:—

The funnel and filtering paper are arranged as already described, but instead of allowing the filtrate to drop directly from the funnel into the test-tube or other vessel, fit to the lower end of the funnel, by means of a short

length of indiarubber tubing, a piece of narrow glass tube bent round upon itself, near its upper extremity, as Fig. 28. The bend insures that the liquid shall entirely fill the tube, and there is therefore formed an unbroken column of liquid in the lower part of the tube, and this column by its weight, reduces the pressure on the lower side of the filter paper, and hence very greatly increases the rate of filtration. In using this arrangement it is important that the paper fits closely to the funnel, otherwise channels are formed for the admission of air, which, of course, altogether spoils the action of the long tube in reducing the pressure below the paper. The tube should be of as great a length as the filter-stand will allow, but a length of a few inches has a remarkable effect in accelerating filtration, especially of gelatinous precipitates like ferric hydroxide, a precipitate which is most tedious to filter by ordinary means. In making the bend in the tube, it will be found best to heat the tube at the proper place in a large flat flame, and, holding each end of the tube in the fingers, when the portion in the flame becomes quite soft, to bring the hands near together, at the same time giving one hand a slight twist. A loop will thus be formed, in a similar manner to the forming of a loop in a short piece of string, if it be held by one hand at each end, and the hands be then brought nearer together. A little practice will make this clearer than any amount of description.

Fig. 28.

To fold a pleated filter paper.—Take a circular piece of filtering paper and fold it in half, then again, and again in half, then open so that its outline is a semicircle; the creases produced by the other foldings are merely to serve as guides. Then, beginning at the straight side (*i.e.*, the diameter of the circle of which the paper now forms half), fold the paper from the centre to the circumference as far as the first crease: then turn the whole paper over, and fold the folded portion back an equal amount on the other side; and so on, until the whole paper is folded into a sector-shaped piece. Press the paper well, so as to

render the creases distinct, and then open it. A conical, pleated filter will thus be formed which, when supported by a funnel, will allow a liquid to flow through with great rapidity.

Filtration.—Take a solution of barium chloride, $BaCl_2$, and add a solution of sodium carbonate, Na_2CO_3, slowly, and finally drop by drop, until a precipitate is no longer formed. Fit a filter-paper into a funnel, and moisten it with a jet of water from the wash-bottle to make it fit closely to the glass. Then support the funnel on a suitable stand, and, having placed a test-tube or small beaker below to receive the *filtrate*, pour a portion of the contents of the test-tube gently on to the side of the filter-paper, taking care not to fill it too full. When this portion has filtered through, add another portion, and so on until the whole is filtered. To *wash* the precipitate on the filter-paper, direct a jet of water on to it so as to wash it down into the apex from the upper edge of the paper, fill up with water, and allow to stand until this water has all filtered through. Then fill up again several times until the washings show no alkaline reaction.

Testing the solubility of precipitates.—Take a small quantity of a solution of silver nitrate, $AgNO_3$, dilute it with water, and add dilute hydrochloric acid, HCl; a white curdy precipitate of silver chloride, $AgCl$, is obtained. Add a solution of ammonium hydroxide, NH_4OH, in excess, and shake up the mixture: the precipitate dissolves, showing that $AgCl$ is soluble in NH_4OH.

This is a convenient method of procedure applicable in most ordinary cases, but it is sometimes advisable to separate the precipitate from the accompanying liquid. This can be done thoroughly by filtration and washing, but more readily thus:—Allow the precipitate to subside, pour off the liquid and fill up with water. Again allow the precipitate to settle down and pour off the water. Repeat this once or twice. This method of washing by *decantation* is applicable only to heavy precipitates.

Marsh's Apparatus.—Take a wide-mouthed bottle of about 8 ounces capacity, fit it with a good cork or indiarubber stopper, in which bore two holes, one for an acid funnel, the other for a delivery tube; this should be bent back horizontally for 3 inches, and then back upon itself and cut off short; then fit it by means of a small cork to a small calcium chloride tube in order to dry the hydrogen. Connect the other end of this tube with a straight piece of hard glass tubing turned up at the end and drawn out to a jet. It is quite common, however, to use an ordinary form of a delivery tube drawn out to a jet. Place zinc (free from arsenic*) in the bottle and pour upon it pure sulphuric acid diluted with about five times its volume of water.

FIG. 29.

Allow the generation of hydrogen to proceed for a few minutes in order to expel all air from the apparatus, and then light the jet.

If the materials are pure, the flame will be almost colourless, and will yield no stain if a piece of porcelain be held in the flame (see p. 137). Great care must be taken that the jet is not lighted too soon; otherwise serious consequences may result, a mixture of hydrogen and air being highly explosive.

Sulphuretted Hydrogen.—This is best used in the form of gas, though a solution in water will suffice if the apparatus for the manufacture of the gas be not readily available.

One form of apparatus consists of two bottles with necks in the side connected together by a piece of india-

* Commercial zinc contains arsenic; it would not therefore afford reliable evidence in testing matter for arsenic (*e.g.* the contents of a stomach where arsenical poisoning has been suspected).

rubber tubing. One bottle is partially, about half, filled with a mixture of fragments of iron sulphide and glass marbles, the latter being used to allow of the free passage of a liquid in the interstices between the pieces of iron sulphide; the other bottle contains dilute hydrochloric acid (1 of strong acid to about 2 or 3 of water). The upper neck of the bottle containing the iron sulphide

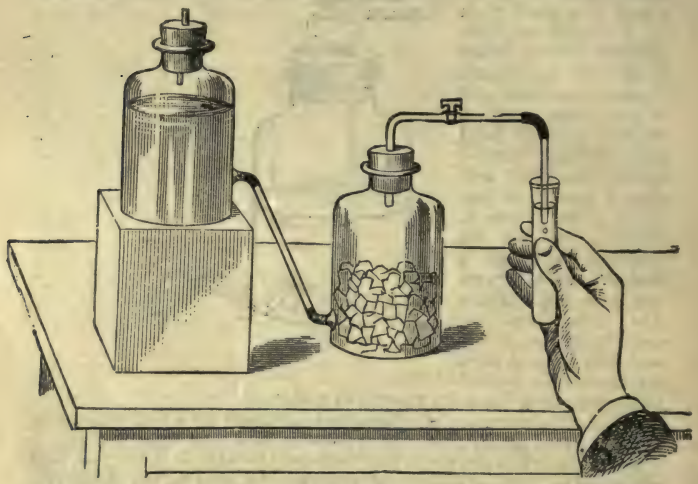

FIG. 30.

is fitted with a cork carrying a tube which is bent at right angles and fitted either with a piece of indiarubber tubing and a pinch-cock, or, better, with a glass stop-cock.

When in use, the acid bottle is raised on a block and a piece of straight glass tube is fitted, by means of a short length of indiarubber tubing, to the delivery tube of the other bottle, and the flow of the gas governed by the stop-cock or pinch-cock. When not in use, the position of the bottles is reversed, when the acid runs away from the iron sulphide, and all action ceases. This arrangement is shown in Fig. 30.

Kipp's Apparatus.—An alternative form of apparatus which is in very common use is shown in Fig. 31. It consists essentially of three bulbous portions, the lower two of which are in one piece and open into each other. The upper bulb terminates below in a tapering tube which reaches nearly to the bottom of the lower bulb; this tube is ground at D so that it fits tightly into the neck of the middle bulb.

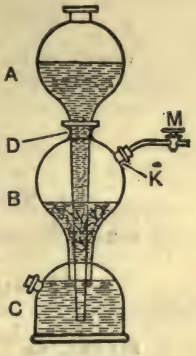

FIG. 31.

A having been placed in position, fragments of ferrous sulphide are introduced into B through K of such size that they will not drop through into C. The tap M is opened and dilute hydrochloric acid is poured into A till C is full and the liquid rises sufficiently high in B to cover the ferrous sulphide. The tap is now closed; the sulphuretted hydrogen produced soon pushes the acid out of B and up into A, thus stopping further action.

When the apparatus is to be brought into use the tap is opened; acid at once runs out of A and rises in B, thus coming in contact with the ferrous sulphide.

CHAPTER II.

REACTIONS OF THE METALS.

GROUP I.

METALS PRECIPITATED AS CHLORIDES.

Group-reagent—HCl.

SILVER, Ag . . . Pp. Silver Chloride, AgCl (*white*).
LEAD, Pb . . . . ,, Lead Chloride, $PbCl_2$,,
MERCURY, Hg′ . . ,, Mercurous Chloride, Hg_2Cl_2 ,,
(*Mercurous*)

SILVER, Ag.

Solution—Silver Nitrate, $AgNO_3$.

1*. The group-reagent, **hydrochloric acid**, HCl, gives a *white curdy* precipitate of AgCl, which becomes violet on exposure to the light: *insoluble in hot water and nitric acid, soluble in ammonia, and in potassium cyanide* with formation of the compounds $AgNH_3Cl$ and $KAg(CN)_2$ respectively.

$$NH_3 + AgCl = AgNH_3Cl.$$
$$2\ KCN + AgCl = KAg(CN)_2 + KCl.$$

2. Potassium chromate, K_2CrO_4, gives, in *neutral* solutions, a *dark red* precipitate of silver chromate, Ag_2CrO_4.

$$K_2CrO_4 + 2\ AgNO_3 = Ag_2CrO_4 + 2\ KNO_3.$$

The precipitate is readily soluble in mineral acids, except

* The most important reactions are numbered in thick type.

hydrochloric acid, which converts it into insoluble silver chloride.

$$Ag_2CrO_4 + 2\ HCl = 2\ AgCl + H_2CrO_4.$$

3. **Potassium cyanide**, KCN, gives a *white curdy* precipitate of silver cyanide, AgCN, very soluble in excess of KCN with formation of $KAg(CN)_2$.

$$AgNO_3 + KCN = AgCN + KNO_3.$$
$$AgCN + KCN = KAg(CN)_2.$$

If the solution is rubbed upon a bright piece of copper, a white stain of silver is produced. This stain does not disappear on heating.

4. **Caustic potash**, KOH, or **caustic soda**, NaOH, gives a dark brown precipitate of silver oxide, Ag_2O.

$$2\ AgNO_3 + 2\ KOH = Ag_2O + H_2O + 2\ KNO_3.$$

The precipitate is soluble in ammonia with formation of $AgNH_3OH$.

$$Ag_2O + 2\ NH_3 + H_2O = 2\ AgNH_3OH.$$

Ammonia gives the same precipitate, soluble of course in excess.

5. **Sulphuretted hydrogen**, H_2S, gives a black precipitate of silver sulphide, Ag_2S, insoluble in dilute acids, except *hot* dilute nitric acid.

6. When a silver salt is mixed with sodium carbonate, Na_2CO_3, and heated on charcoal before the blowpipe, brilliant white malleable beads of silver are obtained. The silver salt is first converted into the carbonate, which is unstable, and readily breaks up into metallic silver, CO_2, and oxygen.

$$4\ AgCl + 2\ Na_2CO_3 = 4\ NaCl + 4\ Ag + 2\ CO_2 + O_2.$$

The beads of silver do not mark paper.

Silver nitrate is the only common soluble salt of silver.

LEAD, Pb.

Solution—Lead Nitrate, $Pb(NO_3)_2$.

1. The group reagent, **hydrochloric acid**, gives a *heavy white crystalline* precipitate of lead chloride, $PbCl_2$: *soluble in hot water*, but crystallizing out on cooling; *insoluble in ammonia*. No precipitate is formed in dilute solutions, because lead chloride is slightly soluble in cold water.

2. **Potassium chromate**, K_2CrO_4, gives a *bright yellow* precipitate of lead chromate, $PbCrO_4$: insoluble in dilute nitric acid and acetic acid. Caustic soda changes the colour of the precipitate from yellow to red, the normal chromate being converted into a basic chromate, $PbCrO_4$, PbO (*chrome red*).

$$2\,PbCrO_4 + 2\,NaOH = PbCrO_4, PbO + Na_2CrO_4 + H_2O.$$

The red precipitate dissolves in excess of caustic soda, forming a red solution. [*Distinction from Bismuth.*]

3. **Potassium iodide**, KI, gives a *golden yellow* precipitate of lead iodide, PbI_2: soluble in boiling water, but crystallizing out in brilliant iridescent scales on cooling.

4. **Sulphuretted hydrogen** produces a *black* precipitate of lead sulphide, PbS. If the solution is strongly acid with HCl, a re dish-brown precipitate is first formed having the composition $(PbS)_2$, $PbCl_2$. Excess of sulphuretted hydrogen decomposes this compound thus—

$$(PbS)_2, PbCl_2 + H_2S = 3\,PbS + 2\,HCl.$$

Lead sulphide is insoluble in cold dilute acids, but dissolves readily in hot dilute nitric acid with formation of lead nitrate, free sulphur and oxides of nitrogen. We may suppose that the first change which takes place is

$$PbS + 2\,HNO_3 = Pb(NO_3)_2 + H_2S.$$

The sulphuretted hydrogen is then oxidized by the excess of nitric acid.

$$3\ H_2S + 2\ HNO_3 = 3\ S + 4\ H_2O + 2\ NO.$$

At the same time a portion of the lead sulphide is oxidized to lead sulphate. If strong nitric acid is used the whole of the sulphide is converted into sulphate.

$$PbS + 8\ HNO_3 = PbSO_4 + 4\ H_2O + 8\ NO.$$

Lead sulphide is insoluble in alkalies and alkaline sulphides.

5. **Dilute sulphuric acid,** H_2SO_4, gives at once in concentrated solutions a *white* precipitate of lead sulphate, $PbSO_4$: precipitation takes place in very dilute solutions only after a time; the addition of alcohol favours the precipitation.

The precipitate is soluble in caustic soda and caustic potash, and also in a solution of ammonium acetate + ammonia.

Lead sulphate also dissolves on long boiling with strong hydrochloric acid.

6. **Potassium hydroxide,** KOH, or **sodium hydroxide,** NaOH, gives a *white* precipitate which at first consists of a basic lead salt *i.e.*, a compound of the normal salt with the hydroxide, $Pb(OH)_2$. As more alkali is added the basic salt is completely converted into the hydroxide, the precipitate remaining white.

Excess of alkali redissolves the precipitate with formation of potassium plumbite, K_2PbO_2, or sodium plumbite, Na_2PbO_2.

$$2\ KOH + 2\ Pb(NO_3)_2 = Pb(NO_3)_2,\ Pb(OH)_2 + 2\ KNO_3.$$
$$2\ KOH + Pb(NO_3)_2,\ Pb(OH)_2 = 2\ Pb(OH)_2 + 2\ KNO_3.$$
$$2\ KOH + Pb(OH)_2 = K_2PbO_2 + 2\ H_2O.$$

Ammonium hydroxide, NH_4OH, behaves in a similar manner except that the precipitate is insoluble in excess.

7. Heat on charcoal with sodium carbonate, Na_2CO_3,

and potassium cyanide, KCN: beads of lead are formed, which are malleable, and mark paper.

Common soluble salts. Lead nitrate, $Pb(NO_3)_2$, and lead acetate, $Pb(C_2H_3O_2)_2$ (sugar of lead), are readily soluble in cold water. Lead chloride, $PbCl_2$, and lead iodide, PbI_2, are sparingly soluble in cold water, but readily soluble in hot water.

MERCURY (*mercurous*), Hg'.

Solution—Mercurous Nitrate, $Hg_2(NO_3)_2$.

1. The group reagent, **hydrochloric acid**, gives a *white* precipitate of mercurous chloride, Hg_2Cl_2 (*calomel*): *insoluble in hot water, blackened by ammonia.*

The blackening on the addition of ammonia is due to the separation of metallic mercury, dimercurammonium chloride, NHg_2Cl, being simultaneously formed.

$$2\,Hg_2Cl_2 + NH_4OH = NHg_2Cl + 2\,Hg + H_2O + 3\,HCl.$$

When mercurous chloride is boiled with strong hydrochloric acid for a long time, it breaks up into mercury (which separates as a black precipitate) and mercuric chloride (which dissolves).

$$Hg_2Cl_2 = Hg + HgCl_2.$$

If nitric acid is substituted for hydrochloric acid complete solution takes place, a mixture of mercuric chloride and nitrate being formed. We may suppose that the mercurous chloride is first broken up into mercury and mercuric chloride, as represented in the above equation, and that the mercury then dissolves in the nitric acid with formation of mercuric nitrate.

$$3\,Hg + 8\,HNO_3 = 3\,Hg(NO_3)_2 + 4\,H_2O + 2\,NO.$$

Aqua regia brings about the solution more readily than nitric acid alone. The nascent chlorine produced by the action of the two acids on each other converts the Hg_2Cl_2 into $HgCl_2$.

2. **Potassium hydroxide**, KOH, or **sodium hydroxide**. NaOH, gives a *black* precipitate of mercurous oxide, Hg_2O.

$$2\,NaOH + Hg_2(NO_3)_2 = Hg_2O + 2\,NaNO_3 + H_2O.$$

[*Distinction from mercuric salts*, which give a *dark yellow* precipitate of mercuric oxide, HgO.]

3. **Stannous chloride**, $SnCl_2$, gives a *grey* precipitate of metallic mercury.

$$SnCl_2 + Hg_2(NO_3)_2 = Hg_2Cl_2 + Sn(NO_3)_2.$$
$$SnCl_2 + Hg_2Cl_2 = 2\,Hg + SnCl_4.$$

[*Distinction from mercuric salts*, see p. 127.]

4. **Sulphuretted hydrogen** produces a *black* precipitate of mercuric sulphide + metallic mercury.

$$Hg_2(NO_3)_2 + H_2S = Hg + HgS + 2\,HNO_3.$$

Mercurous sulphide, Hg_2S, is unknown.

5. When any dry mercurous compound is heated in a tube with powdered charcoal and Na_2CO_3, the metal is reduced and volatilized, and deposited in the cooler parts of the tube in the form of a mirror made up of minute metallic globules.

6.* Acidulate a portion of a solution of any mercurous compound in a tube with nitric acid, and boil with a strip of pure electrolytic copper. A film of mercury is deposited on the copper. When dried between blotting-paper and heated in a tube, the mercury sublimes and the copper resumes its natural colour.

Mercurous nitrate, $Hg_2(NO_3)_2$, is the only common soluble mercurous salt.

* Compare Reinsch's test for arsenic (p. 138).

GROUP II.

METALS PRECIPITATED AS SULPHIDES.

Group-reagent—H_2S in presence of HCl.

DIVISION I.

Metals whose Sulphides are Insoluble in Alkaline Sulphides or Hydrates.

MERCURY, Hg″ (*mercuric*). .	Pp.	**Mercuric Sulphide, HgS** (*black*).
LEAD,* Pb	,,	**Lead Sulphide, PbS** ,,
BISMUTH, Bi	,,	**Bismuth Sulphide, Bi_2S_3** ,,
COPPER, Cu	,,	**Cupric Sulphide, CuS** ,,
CADMIUM, Cd	,,	**Cadmium Sulphide, CdS** (*yellow*).

DIVISION II.

Metals whose Sulphides are Soluble in Alkaline Sulphides or Hydroxides.

TIN, Sn″ (*Stannous*) . . .	Pp.	**Stannous Sulphide, SnS** (*dk. brown*).
Sn^{iv} (*Stannic*) . . .	,,	**Stannic Sulphide, SnS_2** (*yellow*).
ANTIMONY, Sb	,,	**Antimony Sulphide, Sb_2S_3** (*orange*).
ARSENIC, As.	,,	**Arsenic Sulphide, As_2S_3** (*yellow*).

DIVISION I.

MERCURY, Hg″.

Solution—Mercuric Chloride,* $HgCl_2$.

1. The group-reagent,† **sulphuretted hydrogen, H_2S,** added slowly, gives first a *white* precipitate, which, as more of the reagent is added, first becomes *yellow*, then *brown*, and finally *black*. The *white* precipitate is a double compound of HgS and $HgCl_2$ ($HgCl_2$, 2 HgS); the *black* precipitate is HgS. There is some doubt about the composition of the yellow and brown compounds. HgS is insoluble in acids, but is partially converted into

* Lead, as $PbCl_2$, is slightly soluble in cold water, and therefore occurs in Group II. as well as in Group I.

† Sulphuretted hydrogen may be used as a solution in water, or the gas itself may be passed into the solution from a suitable apparatus (see p. 117) until the precipitation is complete. The latter method, where practicable, is preferable.

$Hg(NO_3)_2$, 2 HgS (which is white) by boiling with strong HNO_3. HgS is also insoluble in ammonium sulphide and in caustic alkalies.

2. Stannous chloride, $SnCl_2$, gives, with mercuric salts, a *white* precipitate of mercurous chloride, Hg_2Cl_2, which, on boiling with excess of the reagent, gives grey metallic mercury. If the solution be poured off, and the precipitate boiled with hydrochloric acid, the mercury is obtained in small globules.

$$2\ HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$
$$Hg_2Cl_2 + SnCl_2 = 2\ Hg + SnCl_4.$$

3. Potassium iodide, KI, gives a precipitate which is *yellow* at first, but rapidly changes to *bright scarlet.* The precipitate consists of mercuric iodide, HgI_2.

$$2\ KI + HgCl_2 = HgI_2 + 2\ KCl.$$

The two different colours correspond to two different forms of mercuric iodide. The two forms crystallize in different shapes. At ordinary temperatures the scarlet form is more stable than the yellow, but above 126° C. the reverse is the case.

The precipitate of mercuric iodide is soluble in excess of either the mercuric salt or potassium iodide.

4. Potassium hydroxide, KOH, or **sodium hydroxide**, NaOH, gives in the cold a *yellow* precipitate of mercuric oxide, HgO, insoluble in excess.

$$2\ KOH + HgCl_2 = HgO + H_2O + 2\ KCl.$$

In the heat the precipitate obtained is *red*, but still consists of HgO. The difference in colour is due to difference in the size of the particles.

5. Ammonium hydroxide, NH_4OH, gives a *white* precipitate of *mercurammonium* chloride, NH_2HgCl (*infusible white precipitate*)—

$$2\ NH_4OH + HgCl_2 = NH_2HgCl + NH_4Cl + 2\ H_2O.$$

6. Repeat reactions 5 and 6 for Hg′. Similar results will be obtained.

Mercuric chloride, $HgCl_2$ (corrosive sublimate) is the most important soluble mercuric salt. Mercuric nitrate, $Hg(NO_3)_2$, is also soluble, but the salt is unstable, and when in solution tends to form insoluble basic salts.

LEAD, Pb.

Unless the solution be very dilute, lead is usually detected in Group I. If not so detected, a black precipitate of lead sulphide, PbS, will be obtained on addition of H_2S in Group II., if the solution be not too acid. For this reason, if there is a doubtful indication of a precipitate in Group I., and lead is suspected from preliminary examination (see Chap. iv.), H_2S should be passed through the original solution if that be acid, and not through the portion to which HCl has been added.

[This point is of importance in systematic analysis. On account of the slight solubility of $PbCl_2$ in cold water, Pb is not completely precipitated in Group I.; and if the solution be too acid, or too concentrated, it is not precipitated at all in Group II., and therefore appears in Group III., where it is often mistaken for some other metal.]

For other reactions of Lead, see Group I.

BISMUTH, Bi.

Solution—Bismuth Nitrate, $Bi(NO_3)_3$, dissolved in dilute nitric acid.

1. **Sulphuretted hydrogen** gives a *brownish-black* precipitate of bismuth sulphide, Bi_2S_3.

$$3\,H_2S + 2\,Bi(NO_3)_3 = Bi_2S_3 + 6\,HNO_3.$$

The precipitate is soluble in hot dilute nitric acid, but insoluble in ammonium sulphide and in caustic alkalies.

2. **Water** added in large quantity to a solution of bismuth, to which HCl, or ammonium chloride, NH_4Cl, has first been added, **produces a white precipitate** of a basic chloride, BiOCl, which is insoluble in tartaric acid. [*Distinction from the basic chloride of antimony, SbOCl*, which is soluble in tartaric acid.]

$$BiCl_3 + H_2O = BiOCl + 2\,HCl.$$

3. **Potassium chromate**, K_2CrO_4, gives a *yellow* precipitate of the basic chromate, $Bi_2O(CrO_4)_2$—

$$2\ K_2CrO_4 + 2\ Bi(NO_3)_3 + H_2O = Bi_2O(CrO_4)_2 + 4\ KNO_3 + 2\ HNO_3.$$

The precipitate is soluble in dilute nitric acid, but insoluble in sodium hydroxide. [*Distinction from lead.*]

4. Dilute sulphuric acid, H_2SO_4, gives no precipitate. [*Distinction from lead.*]

5. **Caustic potash**, KOH, gives a white precipitate of bismuth hydroxide, $Bi(OH)_3$, insoluble in excess—

$$3\ KOH + Bi(NO_3)_3 = Bi(OH)_3 + 3\ KNO_3.$$

NaOH and NH_4OH behave in a similar manner.

6. Add caustic potash to stannous chloride, $SnCl_2$, till the precipitate of stannous hydroxide first formed redissolves, forming potassium stannite, K_2SnO_2. Now add a solution of a bismuth salt. A black precipitate of bismuth dioxide, Bi_2O_2, is formed.

$$2\ KOH + SnCl_2 = Sn(OH)_2 + 2\ KCl.$$
$$2\ KOH + Sn(OH)_2 = K_2SnO_2 + 2\ H_2O.$$
$$K_2SnO_2 + 6\ KOH + 2\ Bi(NO_3)_3 = Bi_2O_2 + K_2SnO_3 + 6\ KNO_3 + 3\ H_2O.$$

7. Mix with sodium carbonate, Na_2CO_3, and heat on charcoal before the blowpipe in the reducing flame: brittle metallic beads are obtained, and an *orange-yellow incrustation* is formed on the charcoal.

Most of the soluble bismuth salts are decomposed by water, insoluble basic salts being formed. Bismuth nitrate, $Bi(NO_3)_3$, the commonest salt, dissolves in a small quantity of water, especially if nitric acid is present. A large quantity of water decomposes the salt, and basic bismuth nitrate is formed.

COPPER, Cu.

Solution—Cupric Sulphate, $CuSO_4$.

1. Sulphuretted hydrogen, H_2S, gives a *black* precipitate of cupric sulphide, CuS—

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

The precipitate is soluble in hot dilute nitric acid, but insoluble in hot dilute sulphuric acid. It is *slightly soluble* in ammonium sulphide, but insoluble in caustic alkalies. The moist precipitate rapidly undergoes oxidation to cupric sulphate in the presence of air.

$$CuS + 2\ O_2 = CuSO_4.$$

If potassium cyanide is present sulphuretted hydrogen produces no precipitate with a copper salt. This is because a complex cyanide of potassium and copper, $KCu(CN)_2$, is formed which is not decomposed by H_2S. (See below under 4.)

2. Ammonium hydroxide, NH_4OH, when added in small quantities, produces a *greenish-blue* precipitate of a basic salt, $CuSO_4$, $Cu(OH)_2$, which is readily dissolved in excess of the reagent, forming a splendid *azure-blue liquid;* this coloration is easily perceptible, even if the solution contain only slight traces of copper. The blue solution contains ammonio-cupric sulphate, $CuSO_4$, $(NH_3)_4$, H_2O.

$$2\ CuSO_4 + 2\ NH_4OH = CuSO_4,\ Cu(OH)_2 + (NH_4)_2SO_4.$$
$$CuSO_4 + Cu(OH)_2 + 6\ NH_4OH + (NH_4)_2SO_4 = 2\ CuSO_4,(NH_3)_4,\ H_2O + 6\ H_2O.$$

3. Potassium ferrocyanide, $K_4Fe(CN)_6$ gives a *reddish-brown* precipitate of cupric ferrocyanide, $Cu_2Fe(CN)_6$, in neutral or slightly acid solutions, but not in alkaline solutions.

$$K_4Fe(CN)_6 + 2\ CuSO_4 = Cu_2Fe(CN)_6 + 2\ K_2SO_4.$$

A *brownish colour* is produced in very dilute solutions of

copper salts; it is best seen when the reaction takes place in a watch-glass placed on a sheet of white paper. $K_4Fe(CN)_6$ affords one of the most delicate reactions for copper salts.

4. **Potassium cyanide**, KCN, gives a *greenish-yellow* precipitate of cupric cyanide, $Cu(CN)_2$.

$$2\ KCN + CuSO_4 = Cu(CN)_2 + K_2SO_4.$$

The precipitate rapidly loses cyanogen, forming cuprous cyanide, $Cu_2(CN_2)$.

$$2\ Cu(CN)_2 = Cu_2(CN)_2 + C_2N_2.$$

If excess of potassium cyanide is added the precipitate redissolves, forming a double cyanide of potassium and copper, $KCu(CN)_2$.

$$2\ KCN + Cu_2(CN)_2 = 2\ KCu(CN)_2.$$

As stated above, this compound is not decomposed by sulphuretted hydrogen. The explanation of this is that the ions of the double cyanide are K and $[Cu(CN)_2]$, not K, Cu and (CN), *i.e.*, there are *no free copper ions* (or more correctly only a *very few*). Now it is on the presence of free copper ions that the precipitation of copper by H_2S depends, the sulphur ions of H_2S combining with them to form insoluble CuS.

5. **Caustic potash**, KOH, or **caustic soda**, NaOH, gives a *bulky light blue* precipitate of cupric hydrate, $Cu(OH)_2$.

$$2\ KOH + CuSO_4 = Cu(OH)_2 + K_2SO_4.$$

The precipitate is insoluble in excess. If the mixture is boiled the precipitate becomes black, the cupric hydroxide losing part of its water.

$$3\ Cu(OH)_2 = Cu(OH)_2,\ 2\ CuO + 2\ H_2O.$$

6. If a piece of bright iron be dipped into a cupric solution acidulated with HCl, it becomes coated with copper; if clean iron filings be boiled in the solution, it

will lose its blue colour, the copper being wholly displaced by the iron.

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

7. Mix with sodium carbonate, Na_2CO_3, and potassium cyanide, KCN, and heat before the inner blowpipe flame for some time : red metallic scales of copper are obtained.

Cupric sulphate, $CuSO_4$ (blue vitriol), is the commonest soluble salt of copper. Cupric nitrate, $Cu(NO_3)_2$, and cupric chloride, $CuCl_2$, are also readily soluble.

CADMIUM, Cd.

Solution.—Cadmium Chloride, $CdCl_2$.

1. **Sulphuretted hydrogen,** H_2S, gives a *fine yellow* precipitate of cadmium sulphide, CdS.

$$CdCl_2 + H_2S = CdS + 2\ HCl.$$

The precipitate is soluble in dilute sulphuric acid. [*Distinction from copper.*] The presence of much HCl prevents its formation. It is not soluble in ammonium sulphide or in caustic alkalies.

2. **Potassium hydroxide,** KOH, or **sodium hydroxide,** NaOH, gives a *white* precipitate of cadmium hydroxide, $Cd(OH)_2$.

$$2\ KOH + CdCl_2 = Cd(OH)_2 + 2\ KCl.$$

The precipitate is insoluble in excess.

3. **Ammonium hydroxide,** NH_4OH, gives the same precipitate, *soluble in excess.*

4. **Potassium cyanide,** KCN, gives a *white* precipitate of cadmium cyanide, $Cd(CN)_2$. The precipitate is soluble in excess forming $KCd(CN)_4$.

$$2\ KCN + CdCl_2 = 2\ KCl + Cd(CN)_2.$$
$$2\ KCN + Cd(CN)_2 = K_2Cd(CN)_4.$$

H_2S precipitates cadmium sulphide from this solution, whilst copper sulphide is not precipitated under similar conditions. The explanation is that $K_2Cd(CN)_4$ ionizes partly into K and $[Cd(CN)_4]$ and partly into K, Cd and (CN), *i.e.*, there are some free cadmium ions in solution, and these with the sulphur ions of the H_2S form cadmium sulphide.

5. Mix with sodium carbonate, Na_2CO_3, and heat on charcoal before the inner blowpipe flame: a *brown incrustation* of cadmium oxide, CdO, is obtained. (*This experiment must be carefully performed, for if heated too strongly the oxide is completely volatilized.*)

Cadmium chloride, $CdCl_2$, cadmium sulphate, $CdSO_4$, and cadmium nitrate, $Cd(NO_3)_2$, are common easily soluble salts of cadmium.

DIVISION II.

TIN (*Stannous*), Sn".

Solution—Stannous Chloride, $SnCl_2$.

1. **Sulphuretted hydrogen**, H_2S, gives a *chocolate-coloured* precipitate of stannous sulphide, SnS.

$$SnCl_2 + H_2S = SnS + 2\,HCl.$$

This precipitate is insoluble in *colourless* ammonium sulphide but dissolves in *yellow* ammonium sulphide (which contains sulphur in solution) with formation of ammonium thiostannate, $(NH_4)_2\,SnS_3$.

$$SnS + \underbrace{(NH_4)_2S + S}_{\text{Yellow ammonium sulphide}} = (NH_4)_2\,SnS_3.$$

Addition of acid precipitates *stannic* sulphide, SnS_2, not stannous sulphide, from this solution.

$$(HN_4)_2SnS_3 + 2\,HCl = SnS_2 + 2\,NH_4Cl + H_2S.$$

Stannous sulphide is soluble in caustic potash, a mixture

of potassium or sodium stannite and thiostannite being formed.

$$2\ SnS + 4\ KOH = K_2SnO_2 + K_2SnS_2 + 2\ H_2O.$$

If an acid is added *stannous* sulphide is reprecipitated.

$$K_2SnO_2 + K_2SnS_2 + 4\ HCl = 2\ SnS + 4\ KCl + 2\ H_2O.$$

Stannous sulphide is insoluble in ammonium carbonate. It dissolves in hot strong hydrochloric acid, forming stannous chloride.

2. Mercuric chloride, $HgCl_2$, produces first a *white* precipitate of Hg_2Cl_2, which, when boiled with excess of the solution, becomes of a *greyish-black colour* owing to its reduction to metallic mercury. (For equations see p. 127.)

3. Caustic potash, KOH, and **caustic soda**, NaOH, give a *white* precipitate having the composition SnO, $Sn(OH)_2$. The precipitate is soluble in excess, forming potassium or sodium stannite.

$$2\ SnCl_2 + 4\ KOH = SnO,\ Sn(OH)_2 + 4\ KCl + H_2O.$$
$$SnO,\ Sn(OH)_2 + 4\ KOH = 2\ K_2SnO_2 + 3\ H_2O.$$

Ammonia produces a similar precipitate but it is insoluble in excess.

4. Auric chloride, $AuCl_3$, gives a purple precipitate of doubtful composition (*purple of Cassius*).

5. Add a strip of zinc to a solution acidulated with HCl: it becomes coated with a spongy mass of metallic tin. Platinum-foil, in contact with the strip of zinc, does not become blackened. [*Distinction from copper and antimony.*]

6. Mix with sodium carbonate, Na_2CO_3, and potassium cyanide, KCN, and heat on charcoal before the blowpipe: malleable beads of tin and a white incrustation on charcoal are obtained.

TIN (*Stannic*), Sn^{IV}.

Solution—Stannic Chloride, $SnCl_4$.

1. **Sulphuretted hydrogen**, H_2S, gives a *dull yellow* precipitate of stannic sulphide, SnS_2.

$$SnCl_4 + 2\ H_2S = SnS_2 + 4\ HCl.$$

The precipitate is soluble in *colourless* ammonium sulphide (and, of course, in yellow ammonium sulphide), forming ammonium sulphostannate, $(NH_4)_2SnS_3$.

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

The precipitate also dissolves in caustic alkalies, forming a stannate and a sulphostannate.

$$3\ SnS_2 + 6\ NaOH = 2\ Na_2SnO_3 + Na_2SnS_3 + 3\ H_2O.$$

SnS_2 is insoluble in ammonium carbonate. It dissolves in hot strong hydrochloric acid, forming stannic chloride, $SnCl_4$.

$$SnS_2 + 4\ HCl = SnCl_4 + 2\ H_2S.$$

2. **Caustic potash**, KOH, gives a white precipitate of stannic acid, H_2SnO_3.

$$4\ KOH + SnCl_4 = H_2SnO_3 + 4\ NaCl + H_2O.$$

The precipitate is soluble in excess forming potassium stannate.

$$H_2SnO_3 + 2\ KOH = K_2SnO_3 + 2\ H_2O.$$

NaOH and NH_4OH behave in a similar manner.

Stannic acid is soluble in HCl and HNO_3.

3. Mercuric chloride, $HgCl_2$, gives no precipitate. [*Distinction from stannous salts.*]

4. Reactions 4 and 5 for stannous compounds apply also to stannic compounds.

$SnCl_2$ and $SnCl_4$ are the only common soluble salts of tin.

ARSENIC,* As.

Solution—Arsenious Oxide, As_4O_6, dissolved in dilute HCl (which contains Arsenious Acid, H_3AsO_3).

1. **Sulphuretted hydrogen, H_2S,** gives (*in acid solutions*) a *lemon yellow* precipitate of arsenious sulphide, As_2S_3.

$$3\ H_2S + 2\ H_3AsO_3 = As_2S_3 + 6\ H_2O.$$

The precipitate is soluble in ammonium sulphide, forming ammonium arsenite, $(NH_4)_3AsS_3$, and in caustic alkalies forming a mixture of arsenite and thioarsenite.

$$As_2S_3 + 3\ (NH_4)_2S = 2\ (NH_4)_3AsS_3.$$

$$As_2S_3 + 6\ KOH = \underset{\text{Potassium arsenite}}{K_3AsO_3} + \underset{\text{Potassium thioarsenite}}{K_3AsS_3} + 3\ H_2O.$$

It is also readily soluble in a concentrated solution of ammonium carbonate again forming a mixture of arsenite and thioarsenite.

$$As_2S_3 + 3\ (NH_4)_2CO_3 = \underset{\text{Ammonium arsenite}}{(NH_4)_3AsO_3} + \underset{\text{Ammonium thioarsenite}}{(NH_4)_3AsS_3} + 3\ CO_2.$$

2. **Add cupric sulphate, $CuSO_4$, and then sodium hydroxide, NaOH,** drop by drop, till in excess (to render the solution alkaline): a *fine green* precipitate of arsenite of copper ($CuHAsO_3$) is obtained.

$$H_3AsO_3 + CuSO_4 + 2\ NaOH = CuHAsO_3 + Na_2SO_4 + 2\ H_2O.$$

3. **Marsh's Test.**—Hydrogen is generated from zinc and dilute sulphuric acid, both free from arsenic, in the apparatus described on p. 13, and the jet lit as soon as all the air in the apparatus is displaced by hydrogen. A small quantity of the solution is then poured down the acid

* Arsenic, when present as an arsenate, that is, as As^v, is only precipitated as As_2S_3 *by passing the gas through the solution for some time.* In this form arsenic will be detected as an *acid* (see p. 172).

funnel into the bottle. In a short time arseniuretted hydrogen, AsH_3, is produced and escapes, mixed with a large proportion of hydrogen. The escaping gas now burns with a bluish flame, and fumes of As_4O_6 are evolved. If a cold porcelain dish be held in the flame, a bright black stain of *metallic arsenic* is produced on the dish.

$$6\ AsH_3 + 3\ O_2 = 3\ As + 6\ H_2O.$$

This stain is readily dissolved by a drop of sodium hypochlorite, NaOCl. [*Distinction from antimony.*]

$$2\ As + 5\ NaOCl + 4\ NaOH = 2\ Na_2HAsO_4 + 5\ NaCl + H_2O.$$

If, while the gas is still escaping, the delivery tube be heated by the flame of a Bunsen burner or spirit lamp, at a point a short distance from the jet, a black ring will be produced on the tube just beyond the flame. If the tube be now cut off at this point, and held in a slanting position over a flame so that the ring is gently heated, a sublimate of octahedral crystals will be formed at the jet end of the tube. If the tube, with the sublimate, be dropped into a test-tube containing dilute HCl, the As_4O_6 dissolves and a solution is obtained from which H_2S will precipitate As_2S_3, as in Test 1.

4. Hoffmann's Test.—By the aid of the apparatus employed for the previous test, generate arseniuretted hydrogen, AsH_3; but, instead of burning the gas, pass it by means of a piece of bent tubing into a test-tube containing a solution of silver nitrate. A black precipitate of metallic silver is produced, whilst nitric and arsenious acids remain in solution.

$$AsH_3 + 6\ AgNO_3 + 3\ H_2O = 6\ Ag + H_3AsO_3 + 6\ HNO_3.$$

When the gas has been passing for some minutes, filter the liquid in the tube, add some more silver nitrate and then a few drops of solution of ammonia for the purpose of neutralizing the nitric acid. A *yellow* precipitate of Ag_3AsO_3 is obtained.

$$H_3AsO_3 + 6\ HNO_3 + 3\ AgNO_3 + 9\ NH_4OH = Ag_3AsO_3 + 9\ NH_4NO_3 + 9\ H_2O.$$

5. Fleitmann's Test.—Boil a piece of granulated pure zinc or aluminium foil with a solution of caustic soda: hydrogen is given off. Add a few drops of a solution of As_4O_6; the escaping gas now contains AsH_3, which is recognized by its blackening a piece of filter-paper previously moistened with $AgNO_3$, and held over the mouth of the test-tube. [*Distinction from antimony*, the compounds of which are not reduced in alkaline solutions to SbH_3.]

6. Reinsch's Test.—The solution is mixed with HCl, and boiled with a clean piece of copper-foil. A grey film is deposited on the copper. The copper-foil, having been washed and dried, is then heated in a narrow open tube where the arsenic oxidizes, and arsenious anhydride, As_4O_6, is deposited in the cool part of the tube in octahedral crystals.

7. Mix with sodium carbonate, Na_2CO_3, and powdered charcoal, and heat in a small bulb-tube: a black *lustrous* metallic ring will be produced in the cool part of the tube. This ring, when treated as in Test 3, gives exactly the same results.

Arsenious oxide, As_4O_6, slightly soluble in water, but readily soluble in dilute HCl, is the only common arsenic compound.

ANTIMONY, Sb.

Solution—Antimonious Chloride, $SbCl_3$, dissolved in dilute HCl.

1. Sulphuretted hydrogen, H_2S, gives (*in acid solutions*) an *orange-red* precipitate of antimonious sulphide, Sb_2S_3.

$$3\ H_2S + 2\ SbCl_3 = Sb_2S_3 + 6\ HCl.$$

The precipitate is soluble in ammonium sulphide, forming ammonium thioantimonite, $(NH_4)_3SbS_3$.

$$3\ (NH_4)_2S + Sb_2S_3 = 2\ (NH_4)_3SbS_3.$$

It is also soluble in caustic alkalies, forming an antimonite and a thioantimonite—

$$6\ KOH + Sb_2S_3 = \underset{\text{Potassium antimonite}}{K_3SbO_3} + \underset{\text{Potassium thioantimonite}}{K_3SbS_3} + 3\ H_2O.$$

It is insoluble in ammonium carbonate, but dissolves in boiling strong HCl.

$$Sb_2S_3 + 6\ HCl = 2\ SbCl_3 + 3\ H_2S.$$

2. Water produces a white milkiness due to the precipitate of antimony oxychloride, SbOCl—

$$SbCl_3 + H_2O = SbOCl + 2\ HCl.$$

The precipitate is easily soluble in tartaric acid [*Distinction from bismuth*], forming antimonyl tartrate, $(SbO)_2C_4H_4O_6$.

$$SbOCl + C_4H_6O_6 = (SbO)_2C_4H_4O_6 + 2\ HCl.$$

3. If a piece of platinum-foil and then a strip of zinc be dropped into a solution of antimony acidulated with HCl, so that the metals touch one another, a *brown* or *black* film (metallic antimony) will coat the platinum: free nitric acid must, however, not be present.

4. Marsh's Test.—Apply this test as described for arsenic. On the introduction of the antimony solution to the apparatus, antimoniuretted hydrogen is produced, and the flame becomes bluish-green in colour. A black stain is produced by this flame on cold porcelain, just as in the case of arsenic; but the *stain is less lustrous, and is insoluble in sodium hypochlorite*, NaOCl.

$$4\ SbH_3 + 3\ O_2 = 4\ Sb + 6\ H_2O.$$

5. Hoffmann's Test.—Apply this test as for arsenic. A *black* precipitate is obtained in the solution of silver nitrate: this contains antimony as $SbAg_3$, whilst nitric acid remains in solution.

$$SbH_3 + 3\ AgNO_3 = SbAg_3 + 3\ HNO_3.$$

Filter. Digest the precipitate with tartaric acid. The antimony dissolves with formation of antimonyl tartrate,

leaving the silver. Filter and pass H_2S through the filtrate. An orange precipitate of Sb_2S_3 is formed.

6. Mix with sodium carbonate, Na_2CO_3, and potassium cyanide, KCN, and heat on charcoal before the inner blow-pipe flame: brittle beads of antimony are produced which give off white fumes of antimonious oxide, Sb_4O_6.

Tartar emetic, potassium antimonyl tartrate, $K(SbO)C_4H_4O_6$, and antimonous chloride, $SbCl_3$ (*butter of antimony*), are the commonest antimony compounds. The former is readily soluble in water. The latter dissolves readily in a *small quantity* of water or in dilute HCl; a large quantity of water precipitates SbOCl.

GROUP III.

METALS PRECIPITATED AS HYDROXIDES BY NH_4OH IN THE PRESENCE OF EXCESS OF NH_4Cl.

Group-reagent—NH_4Cl and NH_4OH.*

IRON, Fe''' (*Ferric*). **Pp. Ferric Hydroxide, $Fe(OH)_3$** (*reddish-brown*).

[IRON, Fe'' (Ferrous). Ferrous salts are not completely precipitated by ammonia in the presence of NH_4Cl; hence, before testing for iron in this group, a few drops of nitric acid must be added and the solution boiled in order to convert any *ferrous* salt present into a ferric salt. If iron is found, the original solution must then be tested to discover whether it was initially present as a ferrous or ferric salt.]

CHROMIUM, Cr. Pp. Chromic Hydroxide, $Cr(OH)_3$ (*dark green*).
ALUMINIUM, Al. „ Aluminium Hydrate, $Al(OH)_3$ (*white*).

IRON (*Ferric*), Fe'''.

Solution—Ferric Chloride, $FeCl_3$.

1. Ammonium hydroxide, NH_4OH, gives a *reddish-brown* precipitate of ferric hydroxide, $Fe(HO)_3$.

$$3\ NH_4OH + FeCl_3 = Fe(OH)_3 + 3\ NH_4Cl.$$

* When NH_4Cl and NH_4OH are both to be added to a solution, the NH_4Cl should be added first, because it is often added to prevent the precipitation of hydroxides by the NH_4OH.

The precipitate is insoluble in NH_4Cl. KOH and NaOH give a similar precipitate.

2. Potassium ferrocyanide, $K_4Fe(CN)_6$, gives a *dark blue* precipitate of *Prussian blue*, $Fe_4[Fe(CN)_6]_3$.

$$3\ K_4[Fe(CN)_6] + 4\ FeCl_3 = Fe_4'''[Fe''(CN)_6]_3 + 12\ KCl.$$

3. Potassium ferricyanide, $K_3Fe(CN)_6$, gives *no* precipitate, but a *deep green* (*very dilute solutions*) or *brown coloration.*

4. Potassium sulphocyanate, KCNS, gives the solution a blood-red colour on account of the formation of $Fe(CNS)_3$.

$$3\ KCNS + FeCl_3 = Fe(CNS)_3 + 3\ KCl.$$

The colour of the solution is readily destroyed by a solution of mercuric chloride, $HgCl_2$.

5. Ammonium sulphide, $(NH_4)_2S$, gives a black precipitate of ferrous sulphide, FeS, mixed with sulphur.

$$3\ (NH_4)_2S + 2\ FeCl_3 = 2\ FeS + S + 6\ NH_4Cl.$$

Ferric chloride, $FeCl_3$, and iron alum, $K_2Fe_2(SO_4)_4$, $24H_2O$, are the commonest soluble salts of iron (Fe‴).

IRON (*Ferrous*), Fe″.

Solution—Ferrous Sulphate, $FeSO_4$.

1. Ammonium hydroxide, NH_4OH [also KOH and Na(OH)], gives a *light-coloured* precipitate of ferrous hydroxide, $Fe(OH)_2$, which rapidly turns *dirty green*, and more slowly *reddish-brown*, by reason of the absorption of oxygen, and formation of ferric hydroxide.

$$2\ NH_4OH + FeSO_4 = (NH_4)_2SO_4 + Fe(OH)_2.$$
$$4\ Fe(OH)_2 + O_2 + 2\ H_2O = 4\ Fe(OH)_3.$$

Complete precipitation of ferrous hydroxide by NH_4HO is prevented by the presence of ammonium salts.

2. **Potassium ferrocyanide**, $K_4Fe(CN)_6$, gives a *bluish-white* precipitate which speedily turns blue by absorption of oxygen.

If air is entirely excluded and the ferrous salt is quite free from ferric salt the precipitate is quite white and consists of $K_2Fe''[Fe''(CN)_6]$.

$$K_4[Fe''(CN)_6] + FeSO_4 = K_2Fe''[Fe''(CN)_6] + K_2SO_4.$$

Under ordinary conditions air is always present and so the precipitate is bluish.

3. **Potassium ferricyanide**, $K_3Fe(CN)_6$, gives a *dark blue* precipitate of $Fe_3''[Fe'''CN)_6]_2$ (*Turnbull's blue*). [*Distinction from ferric salts.*]

$$2\ K_3[Fe(CN)_6] + 3\ FeSO_4 = Fe_3''[Fe'''(CN_6)]_2 + 3\ K_2SO_4.$$

4. **Potassium sulphocyanate**, KCNS, produces neither a precipitate nor change of colour when the solution is free from a ferric salt.

5. **Ammonium sulphide**, $(NH_4)_2S$, gives a black precipitate of ferrous sulphide, FeS.

$$(NH_4)_2S + FeSO_4 = FeS + (NH_4)_2SO_4.$$

Ferrous sulphate, $FeSO_4$ (green vitriol), is the common soluble salt of iron, Fe''. Ferrous ammonium sulphate, $Fe_2''(NH_4)_2(SO_4)_2$, is a common double salt soluble in water.

CHROMIUM, Cr.

Solution—Chromic Chloride, $CrCl_3$.

1. **Ammonium hydroxide**, NH_4OH, gives a *dull green* precipitate of chromic hydroxide, $Cr(OH)_3$, with most chromium salts.

$$CrCl_3 + 3\ NH_4OH = Cr(OH)_3 + 3\ NH_4Cl.$$

The precipitate is partially soluble in excess, forming a pinkish solution which contains ammonium chromite, $(NH_4)_2Cr_2O_4$.

$$6\ Cr(OH)_3 + 6\ NH_4OH = 3\ (NH_4)_2Cr_2O_4 + 12\ H_2O.$$

When the liquid is boiled the $Cr(OH)_3$ is completely precipitated, the chromite being decomposed thus—

$$(NH_4)_2Cr_2O_4 + 2\ H_2O = 2\ NH_3 + 2\ Cr(OH)_3.$$

2. Potassium hydroxide, KOH, and sodium hydroxide, NaOH, give the same precipitate soluble in excess of the alkali, and forming a *green* solution.

$$6\ KOH + 6\ Cr(OH)_3 = \underset{\text{Potassium chromite}}{3\ K_2Cr_2O_4} + 12\ H_2O.$$

If the solution is boiled with ammonium chloride the chromite is decomposed, and chromium hydroxide is re-precipitated.

$$K_2Cr_2O_4 + 2\ NH_4Cl + 2\ H_2O = 2\ Cr(OH)_3 + 2\ NH_3 + 2\ KCl.$$

Cautious addition of hydrochloric acid also brings about the reprecipitation of the hydroxide; excess of acid re-dissolves it, forming the chloride.

$$K_2Cr_2O_4 + 2\ HCl + 2\ H_2O = 2\ Cr(OH)_3 + 2\ KCl.$$

3. Chromic compounds may be recognized by converting the chromic oxide into chromic acid. This can be done in several ways:—

(i) By gently warming chromium hydroxide suspended in water with **sodium peroxide, Na_2O_2.**

$$2\ Cr(OH)_3 + 3\ Na_2O_2 = \underset{\text{Sodium chromate}}{2\ Na_2CrO_4} + 2\ NaOH + 2\ H_2O.$$

(ii) By boiling a solution of $CrCl_3$ with NaOH, and **sodium hypochlorite, NaOCl,** or with **bromine water** and **caustic soda** (*i.e.*, NaOBr).

$$Cr(OH)_3 + 3\ NaOCl + 4\ NaOH = 2\ Na_2CrO_4 + 3\ NaCl + 5\ H_2O.$$

(iii) By fusion with alkaline carbonates and nitre. Chromium compounds, when mixed with fusion mixture and nitre, and fused on platinum-foil, give a yellow mass of potassium and sodium chromate.

In each case the chromate can be tested for by acidifying

with acetic acid and then adding lead acetate when a yellow precipitate of lead chromate, $PbCrO_4$, is formed.

$$K_2CrO_4 + Pb(C_2H_3O_2)_2 = PbCrO_4 + 2\ KC_2H_3O_2.$$

4. Chromium compounds give an emerald green borax bead, both in the inner and outer flame.

Chromous chloride, $CrCl_2$, and chromic chloride, $CrCl_3$, are the most important compounds in which chromium occurs as a base. *Chrome alum*, $K_2Cr_2(SO_4)_4$, 24 H_2O, is a common soluble double salt. The *chromates* contain chromium as chromic acid.

ALUMINIUM, Al.

Solution—Alum, $K_2Al_2(SO_4)_4$, 24 H_2O.

1. Ammonium hydroxide, NH_4OH, gives a *white transparent gelatinous* precipitate of aluminium hydroxide, $Al(OH)_3$.

$$K_2Al_2(SO_4)_4 + 3\ NH_4OH = 2\ Al(OH)_3 + K_2SO_4 + 3\ (NH_4)_2SO_4.$$

If a large excess of cold ammonia is added the precipitate redissolves, but on boiling the solution, complete reprecipitation takes place. The presence of ammonium chloride, however, prevents the solution of the hydroxide in cold ammonia.

2. Potassium hydroxide, KOH, or **sodium hydroxide**, NaOH, also precipitates the hydroxide. The precipitate is readily soluble in excess, forming an aluminate.

$$2\ NaOH + 2\ Al(OH)_3 = \underset{\text{Sodium aluminate}}{Na_2Al_2O_4} + 4\ H_2O.$$

Excess of ammonium chloride causes reprecipitation of the hydroxide.

$$Na_2Al_2O_4 + 2\ NH_4Cl + 4\ H_2O = 2\ Al(OH)_3 + 2\ NH_4OH + 2\ NaCl$$

Boiling renders the reprecipitation complete.

The cautious addition of an acid also brings about

this reprecipitation, but if excess of acid is added the hydroxide redissolves (unless the acid is a very weak one, *e.g.*, carbonic acid). Thus in the case, of HCl we have

$$Na_2Al_2O_4 + 2\,HCl + 2\,H_2O = 2\,Al(OH)_3 + 2\,NaCl.$$
$$Al(OH)_3 + 3\,HCl = AlCl_3 + 3\,H_2O.$$

3. **Disodium hydrogen phosphate,** Na_2HPO_4, gives a *white bulky* precipitate of aluminium phosphate, $AlPO_4$ insoluble in NH_4OH and NH_4Cl.

$$2\,Na_2HPO_4 + K_2Al_2(SO_4)_4 = 2\,AlPO_4 + K_2SO_4 + 2\,NaHSO_4 + Na_2SO_4.$$

4. Heat on charcoal before the blowpipe: a white mass is obtained which is highly luminous while hot. Allow to cool, moisten with cobaltous nitrate, and heat again in the inner flame: a *fine blue mass* is obtained. [*Distinction from zinc.*]

The commonest substance containing aluminium is common (potash) alum, which is a soluble double sulphate of potassium and aluminium, $K_2Al_2(SO_4)_4$, $24H_2O$. Ammonium-alum, $(NH_4)_2Al_2(SO_4)_4$, $24H_2O$, is another common alum.

GROUP IV.

Metals precipitated as Sulphides by Ammonium Sulphide, $(NH_4)_2S$, in presence of NH_4OH and NH_4Cl.

Group-reagent—NH_4Cl, NH_4OH, and $(NH_4)_2S$.

NICKEL, Ni . . . **Pp. Nickel Sulphide, NiS** (*black*).
COBALT, Co . . . ,, **Cobalt Sulphide, CoS** (*black*).
MANGANESE, Mn . ,, **Manganese Sulphide, MnS** (*buff*).
ZINC, Zn . . . . ,, **Zinc Sulphide, ZnS** (*white*).

NICKEL, Ni.

Solution—Nickel Sulphate, $NiSO_4$.

[*Note that the colour of the solution is green. All aqueous solutions of nickel salts are of a greenish colour.*]

1. **Ammonium sulphide,** $(NH_4)_2S$, gives a ***black*** precipitate

of nickel sulphide, NiS : slightly soluble in excess if *yellow* ammonium sulphide is used, producing a dark brown liquid.

$$(NH_4)_2S + NiSO_4 = NiS + (NH_4)_2SO_4.$$

The precipitate is insoluble in acetic acid and practically so in dilute HCl. It dissolves slowly in hot concentrated HCl, rapidly in HCl + a crystal of $KClO_3$, and in aqua regia. If acetic acid is added to the black liquid referred to above the dissolved nickel sulphide is reprecipitated.

2. **Potassium hydroxide**, KOH, or **sodium hydroxide**, NaOH, gives an apple-green precipitate of $Ni(OH)_2$.

$$2\,KOH + NiSO_4 = Ni(OH)_2 + K_2SO_4.$$

The precipitate is insoluble in excess.

3. **Ammonium hydroxide**, NH_4OH, produces *in neutral solution* the same precipitate which, however, dissolves in excess of the reagent to a blue liquid, containing the compound $NiSO_4,4\,NH_3$. The precipitate is not formed in the presence of NH_4Cl or other ammonium salts. On this account there is no precipitate when ammonium hydroxide is added to an acid solution of a nickel salt; an ammonium salt is formed and prevents the precipitation.

4. **Potassium cyanide**, KCN, gives a *yellowish-green* precipitate of nickel cyanide, $Ni(CN)_2$: soluble in excess, giving a brownish-yellow solution, containing a double cyanide of nickel and potassium, $K_2Ni(CN)_4$.

$$2\,KCN + NiSO_4 = Ni(CN)_2 + K_2SO_4.$$
$$2\,KCN + Ni(CN)_2 = K_2Ni(CN)_4.$$

The solution undergoes no change when boiled in air. On adding caustic soda and bromine (*i.e.*, NaOBr)* or

* When bromine is added to caustic soda in the cold sodium hypobromite, NaOBr, is formed:

$$2\,NaOH + Br_2 = NaBr + NaOBr + H_2O.$$

sodium hypochlorite (NaOCl) and warming gently, a black precipitate of $Ni_2(OH)_6$ is obtained.

$$2\ K_2Ni(CN)_4 + NaOBr + NaOH + H_2O = Ni_2(OH)_6 + 4\ KCN + 4\ NaCN + NaBr.$$

5. **Potassium nitrite + acetic acid** gives no precipitate. [*Distinction from cobalt.*]

6. Heated on a borax bead, in the outer flame, compounds of nickel yield an intensely coloured bead, which appears *hyacinth-red* to *violet-brown* when *hot*, and *yellowish* to *sherry-red* when *cold*, according to the quantity of nickel present.

Nickel sulphate, $NiSO_4$, nickel chloride, $NiCl_2$, and nickel nitrate, $Ni(NO_3)_2$, are the commonest soluble nickel salts. They are all of a green colour and more or less deliquescent.

COBALT, Co.

Solution—Cobalt Nitrate, $Co(NO_3)_2$.

[*Note that the colour of the solution is a pale red. All aqueous solutions of cobalt salts are of a reddish colour.*]

1. **Ammonium sulphide**, $(NH_4)_2S$, gives a *black* precipitate of cobalt sulphide, CoS, insoluble in excess.

$$(NH_4)_2S + Co(NO_3)_2 = 2\ NH_4NO_3 + CoS.$$

The precipitate is insoluble in acetic acid and practically so in dilute hydrochloric acid, but dissolves slowly in the hot strong acid. It is readily soluble in HCl + a crystal of $KClO_3$, and in aqua regia.

2. **Potassium hydroxide**, KOH, or **sodium hydrate**, NaOH, gives a precipitate of a *blue* basic salt, which on exposure to the air becomes *olive-green*, owing to the absorption of oxygen. When heated, a rose-red cobaltous hydroxide, $Co(OH)_2$, is obtained, which contains usually a small quantity of dark brown cobaltic hydroxide, $Co_2(OH)_6$. The precipitate is dissolved by ammonium carbonate to an intensely violet-red fluid.

3. Ammonium hydroxide, NH_4OH, gives *in neutral solution* a *bluish-green* precipitate of a basic salt readily soluble in excess. The precipitate is not formed in the presence of ammonium salts, (*e.g.*, ammonium chloride), and so when ammonium hydroxide is added to an *acid solution* of a cobalt salt, no precipitate is formed (*cf.* the similar behaviour of nickel, p. 146).

4. Potassium cyanide, KCN, produces a *reddish-brown* precipitate of cobaltous cyanide, $Co(CN)_2$, which is redissolved in excess of KCN, forming potassium cobaltous cyanide, $K_4Co(CN)_6$.

$$2\ KCN + Co(NO_3)_2 = Co(CN)_2 + 2\ KNO_3.$$
$$4\ KCN + Co(CN)_2 = K_4Co(CN)_6.$$

When this solution is boiled it absorbs oxygen from the air and is converted into potassium cobalticyanide, $K_3Co(CN)_6$.

$$4\ K_4Co(CN)_6 + O_2 + 2\ H_2O = 4\ K_3Co(CN)_6 + 4\ KOH.$$

The oxidation takes place more rapidly if a trace of free acid is present, so that a few drops of acetic acid should be added before boiling. If now this solution is allowed to cool and then gently warmed with caustic soda and bromine (NaOBr) or with sodium hypochlorite (NaOCl) *no* precipitate is formed, as these reagents do not decompose potassium cobalticyanide at a gentle heat. [*Distinction from nickel.*]

5. Potassium nitrite in the presence of *free* **acetic acid** gives a yellow precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$. [*Distinction from nickel.*]

$$Co(NO_3)_2 + 7\ KNO_2 + 2\ C_2H_4O_2 = K_3Co(NO_2)_6 + 2\ KNO_3 + 2\ KC_2H_3O_2 + H_2O + NO.$$

6. The borax bead is coloured *blue* in the outer and inner flame by cobalt compounds.

Cobaltous sulphate, $CoSO_4$, cobaltous nitrate, $Co(NO_3)_2$, and cobaltous chloride, $CoCl_2$, are the most important of the soluble cobalt salts.

MANGANESE, Mn.

Solution—Manganous Sulphate, $MnSO_4$.

1. **Ammonium sulphide**, $(NH_4)_2S$, gives a *flesh-coloured* precipitate of manganese sulphide, MnS. [*Distinction from* Ni, Co, *and* Zn.]

$$MnSO_4 + (NH_4)_2S = MnS + (NH_4)_2SO_4$$

The precipitate is readily soluble in dilute mineral acids, and is even soluble in acetic acid. [*Distinction from* Ni, Co, *and* Zn.]

$$MnS + 2\,HC_2H_3O_2 = H_2S + Mn(C_2H_3O_2)_2.$$

2. **Sodium hydroxide**, NaOH, or **potassium hydroxide**, KOH, gives a *white* precipitate of manganous hydrate, $Mn(OH)_2$, insoluble in excess. The precipitate speedily absorbs oxygen from the air, and turns *dark brown* with the formation of the hydrated manganic oxide, Mn_2O_3, H_2O, which is insoluble in NH_4Cl.

$$2\,NaOH + MnSO_4 = Mn(OH)_2 + Na_2SO_4.$$
$$4\,Mn(OH)_2 + O_2 = 2\,Mn_2O_3,\,H_2O + 2\,H_2O.$$

3. **Ammonium hydroxide**, NH_4OH, produces the same precipitate, except when ammonium salts are present, when the precipitation is prevented.

[On adding NH_4Cl and NH_4OH to a solution of a manganese salt, a soluble double chloride of ammonium and manganese, $2\,NH_4Cl, MnCl_2$, is formed. On exposure to air, this solution is gradually oxidized, and the manganese precipitated as Mn_2O_3, H_2O. For this reason manganese may be precipitated in Group III., *but the precipitation does not take place until after exposure to the air for some time.* Ferric hydroxide is precipitated *immediately.*]

4. Fuse a *very small* quantity of a manganese salt with fusion mixture and a little potassium nitrate, KNO_3, on a piece of platinum-foil. A *deep green mass* remains. This

mass is a mixture of potassium and sodium manganates, K_2MnO_4 and Na_2MnO_4.

If the mixture is treated with a small quantity of water it forms a *deep green* solution of the manganates. Excess of water causes the colour of the solution to change to *pale pink*, the manganates being converted partly into permanganates ($KMnO_4$, $NaMnO_4$), and partly into hydrated manganic oxide, Mn_2O_3, H_2O.

$$8\ K_2MnO_4 + 6\ H_2O = 6\ KMnO_4 + Mn_2O_3, H_2O + 10\ KOH.$$

The permanganates cause the pink colour; the Mn_2O_3, H_2O falls as a brown precipitate. The conversion of manganates into permanganates is also readily brought about by the action of an acid (even carbonic acid).

$$8\ K_2MnO_4 + 5\ CO_2 + H_2O = 6\ KMnO_4 + Mn_2O_3, H_2O + 5\ K_2CO_3$$

$$8\ K_2MnO_4 + 5\ H_2SO_4 = 6\ KMnO_4 + Mn_2O_3, H_2O + 5\ K_2SO_4 + 4\ H_2O.$$

5. In the outer flame the borax bead is coloured *amethyst* when cold. In the inner flame the bead becomes nearly colourless.

The most important salts of manganese are manganous sulphate, $MnSO_4$, and manganous chloride, $MnCl_2$. Of these the sulphate is the more commonly met with. The manganic salts are very unstable.

ZINC, Zn.

Solution—Zinc Sulphate, $ZnSO_4$.

1. **Ammonium sulphide**, $(NH_4)_2S$, gives a *white* precipitate of zinc sulphide, ZnS.

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4.$$

The precipitate is soluble in dilute mineral acids but not in acetic acid. [*Distinction from Mn.*]

2. Potassium hydroxide, KOH, or **sodium hydroxide**, NaOH, gives a white *gelatinous* precipitate of zinc hydroxide, $Zn(OH)_2$, soluble in excess forming potassium zincate, K_2ZnO_2, or sodium zincate, Na_2ZnO_2.

$$2\ KOH + ZnSO_4 = Zn(OH)_2 + K_2SO_4.$$
$$Zn(OH)_2 + 2\ KOH = K_2ZnO_2 + 2\ H_2O.$$

The precipitation is incomplete in the presence of NH_4Cl, the zinc being converted into the double salt, $2\ NH_4Cl, ZnCl_2$, which is not completely decomposed by caustic alkalies.

$$ZnSO_4 + 4\ NH_4Cl = 2\ NH_4Cl, ZnCl_2 + (NH_4)_2SO_4.$$

This behaviour is quite different from that of aluminium, for it will be remembered that NH_4Cl reprecipitates aluminium hydroxide from a solution of sodium aluminate (see p. 40).

3. Ammonium hydroxide, NH_4OH, produces the same precipitate, soluble in excess forming ammonium zincate, $(NH_4)_2ZnO_2$. In the presence of NH_4Cl, however, no precipitate is formed, the double salt $NH_4Cl, ZnCl_2$ not being decomposed by ammonia.

4. Potassium ferrocyanide, $K_4Fe(CN)_6$, gives a *white* precipitate of $Zn_2Fe(CN)_6$.

$$K_4Fe(CN)_6 + 2\ ZnSO_4 = Zn_2Fe(CN)_6 + 2\ K_2SO_4.$$

The precipitate is insoluble in dilute acids.

5. Heat some of the dry salt on charcoal: a mass of zinc oxide, ZnO, remains, which is *yellow when hot*, and *white when cold*. Allow to cool, moisten with a drop of cobaltous nitrate, $Co(NO_3)_2$, and again heat. The mass now becomes *green*.

The more commonly occurring zinc salts are the sulphate (*white vitriol*), $ZnSO_4, 7\ H_2O$, the chloride, $ZnCl_2$, and the acetate, $Zn(C_2H_3O_2)_2$.

GROUP V.

METALS PRECIPITATED AS CARBONATES BY AMMONIUM CARBONATE, $(NH_4)_2CO_3$, IN THE PRESENCE OF NH_4Cl AND NH_4OH.

Group-reagent—NH_4Cl, NH_4OH, $(NH_4)_2CO_3$.

BARIUM, Ba . . . **Pp. Barium Carbonate, $BaCO_3$** (*white*).
STRONTIUM, Sr. . . ,, Strontium Carbonate, $SrCO_3$,,
CALCIUM, Ca . . . ,, Calcium Carbonate, $CaCO_3$,,

BARIUM, Ba.

Solution—Barium Chloride, $BaCl_2$.

1. **Ammonium carbonate,** $(NH_4)_2CO_3$, gives a *white* precipitate of barium carbonate.

$$(NH_4)_2CO_3 + BaCl_2 = BaCO_3 + 2\,NH_4Cl.$$

2. **Dilute sulphuric acid,** H_2SO_4, **and all soluble sulphates,** give immediately a *heavy white granular* precipitate of barium sulphate, $BaSO_4$, even from very dilute solutions of barium salts.

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2\,HCl.$$

The precipitate is insoluble in acids except hot strong sulphuric acid, which slowly converts it into the acid sulphate, $BaH_2(SO_4)_2$; it is also insoluble in alkalies and in ammonium sulphate.

Solutions of strontium or calcium sulphate—two sulphates which are but slightly soluble in water—constitute the most delicate test for barium.

3. **Potassium chromate,** K_2CrO_4, gives a *lemon-yellow* precipitate of barium chromate, $BaCrO_4$; soluble in nitric and hydrochloric acids, but insoluble in acetic acid. [*Distinction from strontium and calcium salts.* See pp. 49, 50.]

$$K_2CrO_4 + BaCl_2 = BaCrO_4 + 2\,KCl.$$

4. **Hydrofluosilicic acid,** H_2SiF_6, produces a *colourless*

crystalline precipitate of barium silicofluoride, $BaSiF_6$. [*Distinction of barium from strontium and calcium salts*, which give no precipitate.]

$$H_2SiF_6 + BaCl_2 = BaSiF_6 + 2\ HCl.$$

The precipitate subsides quickly, especially when an equal bulk of alcohol is added. This is because the precipitate is insoluble in alcohol whereas it is slightly soluble in water. It is also slightly soluble in dilute acids.

5. **Ammonium oxalate**, $(NH_4)_2C_2O_4$, gives a *white* precipitate of barium oxalate, BaC_2O_4, sparingly soluble in acetic acid, readily in HCl.

$$(NH_4)_2C_2O_4 + BaCl_2 = BaC_2O_4 + 2\ NH_4Cl.$$

6. Barium compounds, when heated in the lower part of a Bunsen flame, colour the upper part of the flame yellowish-green.

Barium chloride, $BaCl_2$, and barium nitrate, $Ba(NO_3)_2$, are the commonest soluble salts of barium.

STRONTIUM, Sr.

Solution—Strontium Chloride, $SrCl_2$.

1. **Ammonium Carbonate**, $(NH_4)CO_3$, gives a *white* precipitate of strontium carbonate, $SrCO_3$.

$$(NH_4)_2CO_3 + SrCl_2 = SrCO_3 + 2\ NH_4Cl.$$

2. **Dilute sulphuric acid**, H_2SO_4, **and all soluble sulphates**, produce a *white* precipitate of strontium sulphate, $SrSO_4$.

$$H_2SO_4 + SrCl_2 = SrSO_4 + 2\ HCl.$$

In dilute solutions the precipitate only appears after some time, more especially when calcium sulphate is used as the precipitant: heat favours the precipitation.

3. **Potassium chromate**, K_2CrO_4, gives no precipitate

unless the solution is *strong*, when a yellow precipitate of strontium chromate, $SrCrO_4$, is formed.

$$K_2CrO_4 + SrCl_2 = SrCrO_4 + 2\,KCl.$$

The precipitate is soluble in acetic acid. [*Cf.* barium, p. 152.]

4. **Hydrofluosilicic acid**, H_2SiF_6 gives no precipitate. [*Distinction from barium.*]

5. Strontium compounds colour the flame an *intense crimson.*

Strontium nitrate, $Sr(NO_3)_2$, and chloride, $SrCl_2$, are the commonest soluble compounds of strontium.

CALCIUM, Ca.

Solution—Calcium Chloride, $CaCl_2$.

1. **Ammonium carbonate**, $(NH_4)_2CO_3$, gives a *white* precipitate of calcium carbonate, $CaCO_3$.

$$(NH_4)_2CO_3 + CaCl_2 = CaCO_3 + 2\,NH_4Cl.$$

2. **Ammonium oxalate**, $(NH_4)_2C_2O_4$, gives a *white powdery* precipitate of calcium oxalate, CaC_2O_4, even in largely diluted solutions.

$$(NH_4)_2C_2O_4 + CaCl_2 = CaC_2O_4 + 2\,NH_4Cl.$$

The precipitate is insoluble in acetic and oxalic acids, but is readily soluble in nitric and hydrochloric acids.

3. **Dilute sulphuric acid or soluble sulphates** give, *from concentrated solutions*, a white precipitate of calcium sulphate, $CaSO_4$, which is slightly soluble in water.

$$H_2SO_4 + CaCl_2 = CaSO_4 + 2\,HCl.$$

4. **Potassium chromate**, K_2CrO_4, gives no precipitate. [*Distinction from barium.*]

5. **Hydrofluosilicic acid**, H_2SiF_6, gives no precipitate. [*Distinction from barium.*]

6. Calcium compounds colour the flame a yellowish-red.

The chloride and sulphate are the compounds of calcium most commonly met with.

GROUP VI.

No Group-reagent.

MAGNESIUM, Mg.	**SODIUM, Na.**
POTASSIUM, K.	**AMMONIUM, NH_4.**

MAGNESIUM, Mg.

Solution—Magnesium Sulphate, $MgSO_4$.

1. **Ammonia,** NH_4OH, gives a white precipitate of magnesium hydroxide, $Mg(OH)_2$.

$$2\,NH_4OH + MgSO_4 = Mg(OH)_2 + (NH_4)_2\,SO_4.$$

In the presence of NH_4Cl no precipitate is formed because of the formation of the soluble double chloride of ammonium and magnesium, $2\,NH_4Cl$, $MgCl_2$. This compound is not decomposed by ammonia.

If ammonia is added to magnesium *chloride* only *half* the magnesium is precipitated as the hydroxide; the other half is converted into the double chloride.

$$2\,NH_4OH + 2\,MgCl_2 = 2\,NH_4Cl,\,MgCl_2 + Mg(OH)_2.$$

[The double chloride formed in the presence of NH_4Cl is not precipitated by $(NH_4)_2CO_3$; hence magnesium is not precipitated in Group V., provided a sufficient quantity of NH_4Cl be present.]

2. **Caustic potash,** KOH, precipitates the hydroxide, $Mg(OH)_2$, unless ammonium chloride is present. NaOH, $Ba(OH)_2$ and $Ca(OH)_2$ give the same precipitate.

3. **Disodium hydrogen phosphate,** Na_2HPO_4, in the presence of NH_4OH and NH_4Cl, gives a *white crystalline* precipitate of ammonium magnesium phosphate, $MgNH_4PO_4$.

$$MgSO_4 + Na_2HPO_4 + 2\,NH_4Cl + NH_4OH = MgNH_4PO_4 + (NH_4)_2SO_4 + 2\,NaCl + H_2O.$$

The separation from a dilute solution of a salt of magnesium is promoted by heating gently and stirring with a glass rod. Very dilute solutions give a precipitate only after standing some hours in a warm place.

4. Heat strongly before the blowpipe on charcoal: moisten the residue with cobaltous nitrate, and again heat: a *pale pink mass* will be obtained. [*Distinction from zinc and aluminium.*]

Magnesium sulphate, $MgSO_4$, and magnesium chloride, $MgCl_2$, are the commonest soluble magnesium compounds.

POTASSIUM, K.

Solution—Potassium Chloride, KCl

1. Place a few drops of the solution on a watch-glass, and add to it two or three drops of platinic chloride, $PtCl_4$, a little HCl, and then a few drops of alcohol. If the solution is concentrated, a *dense yellow crystalline* precipitate of the double chloride, K_2PtCl_6, is at once formed.

$$2\ KCl + PtCl_4 = K_2PtCl_6.$$

If the solution be dilute, the precipitate is obtained only after some time.

Its formation can be hastened by rubbing the bottom of the watch-glass with a glass rod. The precipitate forms along the lines where the rod comes in contact with the watch-glass. In very dilute solutions no precipitate is obtained.

Note.—Potassium iodide behaves abnormally. It gives a brown coloration owing to the liberation of iodine, but no precipitate, if only sufficient $PtCl_4$ is present to oxidize the KI. (If more than this is present it will combine with the KCl, produced as shown in the following equation, and a precipitate will be formed.)

$$2\ KI + PtCl_4 = 2\ KCl + PtCl_2 + I_2.$$

The solution should be boiled for a few minutes with the

addition of nitric acid so as to expel the iodine. The addition of $PtCl_4$ will then produce a precipitate of K_2PtCl_4.

2. Tartaric acid gives in concentrated neutral or slightly acid solutions a *white crystalline* precipitate of acid potassium tartrate, $KHC_4H_4O_6$ (cream of tartar).

$$KCl + H_2C_4H_4O_6 = KHC_4H_4O_6 + HCl.$$

Shaking or stirring favours the precipitation.

3. Place a few drops of the solution on a watch-glass and add some sodium cobaltinitrite, $Na_3Co(NO_2)_6$. Stir up with a glass rod. A *yellow* precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$ forms along the lines where the rod touches the glass.

$$3\,KCl + Na_3Co(NO_2)_6 = K_3Co(NO_2)_6 + 3\,NaCl.$$

4. Potassium compounds colour the flame *violet*. Owing to the presence of traces of sodium in all potassium salts, this flame test is not always distinct. By looking at the flame through a piece of blue cobalt glass the potassium flame can be distinguished in the presence of sodium, but this method is not very reliable, and, unless the potassium flame is very distinct, its presence will need careful confirmation in the wet way.

The nitrate, chloride, bromide, iodide, carbonate, and sulphate are the most common potassium compounds.

SODIUM, Na.

Solution—Sodium Chloride, NaCl.

1. Platinic chloride, $PtCl_4$, and tartaric acid give *no* precipitate.

2. Potassium pyroantimonate, $K_2H_2Sb_2O_7$, gives a *white crystalline* precipitate of sodium pyroantimonate, $Na_2H_2Sb_2O_7$, from *concentrated* neutral or alkaline solutions.

$$K_2H_2Sb_2O_7 + 2\,NaCl = Na_2H_2Sb_2O_7 + 2\,KCl.$$

3. Place a few drops of the solution on a watch-glass and add a strong solution of potassium dihydroxytartrate, $K_2C_4H_4O_8$. Rub a glass rod along the bottom of the watch-glass. A white precipitate of sodium dihydroxytartrate, $Na_2C_4H_4O_8$, forms in lines.

$$K_2C_4H_4O_8 + 2\ NaCl = Na_2C_4H_4O_8 + 2\ KCl.$$

4. Sodium compounds colour the flame an *intense golden-yellow.*

[This test is the most reliable for sodium, but it must be remembered that traces of sodium are always present, so that a faint yellow coloration of the flame may in general be neglected. When sodium is present in quantity, the colour is characteristic and *very* intense.]

All sodium compounds are soluble in water, the most common being the chloride, sulphate, nitrate, carbonate, and phosphate.

AMMONIUM, NH_4.

Solution—Ammonium Chloride, NH_4Cl.

1. Platinic chloride, $PtCl_4$, produces in concentrated neutral or acid solutions a *dense yellow* precipitate of the double chloride, $(NH_4)_2PtCl_6$.

$$2\ NH_4Cl + PtCl_4 = (NH_4)_2\ PtCl_6.$$

The experiment should be carried out as in the corresponding case of potassium (p. 52).

2. Add caustic da, NaOH, or caustic potash, KOH, and heat gently. Ammonia, NH_3, is given off, and is readily recognized by smell, action on litmus paper, and by fuming when a glass rod dipped in HCl is brought near it.

$$NaOH + NH_4Cl = NaCl + NH_3 + H_2O.$$

3. Heat some dry ammonium chloride in a test-tube: a white sublimate is formed in the upper part of the tube. All ammonium salts are either volatilized or decomposed by heat.

4. *Nessler's solution* (potassic mercuric iodide, $HgI_2,2KI$,

+ NaOH) gives a *brown* precipitate of NHg_2I, H_2O, or a *yellowish-brown coloration*, according to the amount of ammonia present.

$$2\,HgI_2 + 2\,KI + 4\,NaOH + NH_4Cl = NHg_2I.H_2O + 3\,H_2O + 4\,KI + 3\,NaI + NaCl.$$

This reaction is too delicate for the analysis of ordinary salts, and should only be used for detecting traces of ammonia.

The most common salts of ammonium are the chloride, carbonate, sulphate, bromide, and nitrate.

CHAPTER III.

REACTIONS OF THE ACIDS.

SULPHURIC ACID, H_2SO_4.

Solution—Potassium Sulphate, K_2SO_4.

1. Barium chloride, $BaCl_2$, gives a *heavy white powdery* precipitate of barium sulphate, $BaSO_4$, insoluble in HCl. (See p. 152).

2. Lead acetate, $Pb(C_2H_3O_2)_2$, gives a *heavy white* precipitate of lead sulphate, $PbSO_4$. (See p. 123.)

SULPHUROUS ACID, H_2SO_3.

Solution—Sodium Sulphite, Na_2SO_3.

1. Add HCl, and, if necessary, heat: the smell of burning sulphur is perceptible, SO_2 being evolved *without* the precipitation of sulphur. [*Distinction from thiosulphates.*]

$$Na_2SO_3 + 2\ HCl = 2\ NaCl + H_2O + SO_2.$$

2. To some pieces of granulated zinc in a test-tube add a little hydrochloric acid till a brisk effervescence takes place; then pour in some of the liquid to be tested, and hold a piece of filter-paper moistened with lead acetate in the escaping gas. Any sulphite present will be reduced by the hydrogen and converted into sulphuretted

hydrogen, H_2S, which will stain the paper black with lead sulphide.

$$H_2SO_3 + 6\,H = H_2S + 3\,H_2O.$$
$$H_2S + Pb(C_2H_3O_2)_2 = PbS + 2\,HC_2H_3O_2.$$

3. **Barium chloride,** $BaCl_2$, gives a *white* precipitate of $BaSO_3$, *soluble* in HCl.

$$BaCl_2 + Na_2SO_3 = BaSO_3 + 2\,NaCl.$$

Most sulphites contain small quantities of sulphate (from oxidation), and hence the precipitate with $BaCl_2$ is usually not completely soluble in HCl.

4. **Silver nitrate,** $AgNO_3$, gives a *white* precipitate of silver sulphite, Ag_2SO_3.

$$2\,AgNO_3 + Na_2SO_3 = Ag_2SO_3 + 2\,NaNO_3.$$

If the mixture is heated the precipitate becomes *black*, metallic silver being formed.

$$Ag_2SO_3 + H_2O = 2\,Ag + H_2SO_4.$$

5. **Lead acetate,** $Pb(C_2H_3O_2)_2$, gives a *white* precipitate of lead sulphite, $PbSO_3$, which remains unchanged on heating. [*Distinction from thiosulphates.*]

$$Pb(C_2H_3O_2)_2 + Na_2SO_3 = PbSO_3 + 2\,NaC_2H_3O_2.$$

THIOSULPHURIC ACID, $H_2S_2O_3$.

Solution—Sodium Thiosulphate, $Na_2S_2O_3$.

1. **Hydrochloric acid** or **dilute sulphuric acid** gives, on warming, a smell of SO_2, and a *whitish-yellow* precipitate of sulphur.

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + H_2O + SO_2 + S.$$

2. **Silver nitrate,** $AgNO_3$, added gradually, in excess, gives, after some time, a *white* precipitate of silver thiosulphate, $Ag_2S_2O_3$.

$$2\,AgNO_3 + Na_2S_2O_3 = Ag_2S_2O_3 + 2\,NaNO_3.$$

The precipitate slowly decomposes, becoming *yellowish-brown* and then *black*, forming silver sulphide, Ag_2S, thus—

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

3. **Lead acetate**, $Pb(C_2H_3O_2)_2$, gives a *white* precipitate of lead thiosulphate, PbS_2O_3, which becomes *black* on boiling, the thiosulphate being converted into sulphide. [*Distinction from sulphites.*]

$$Pb(C_2H_3O_2)_2 + Na_2S_2O_3 = PbS_2O_3 + 2\ NaC_2H_3O_2.$$
$$PbS_2O_3 + H_2O = PbS + H_2SO_4.$$

HYDROSULPHURIC ACID, H_2S.

Solution—Ammonium Sulphide, $(NH_4)_2S$.

1. Heat with HCl: sulphuretted hydrogen gas is given off, which is known by its characteristic odour and the black stain it produces on paper moistened with lead acetate; and most soluble sulphides, since they contain persulphides, give a white precipitate of sulphur.

2. Lead acetate gives a *black* precipitate of lead sulphide, PbS.

3. Soluble cadmium salts give a *fine yellow* precipitate of cadmium sulphide, CdS.

4. Heat a dry sulphide in a piece of glass tubing held obliquely over a flame: in general, sulphur dioxide gas, which may be recognized by its odour, is given off.

Tests 2 and 3 are applicable to the detection of H_2S as an aqueous solution or as a soluble sulphide.

Note.—All salts of sulphur acids may be detected thus:—Fuse with Na_2CO_3 on charcoal in the inner blowpipe flame. The sulphur is converted into sodium sulphide. Thus suppose calcium sulphite, $CaSO_3$, is the salt used. This is first reduced to calcium sulphide, CaS, by the char-

coal, and then sodium sulphide is formed by double decomposition with the sodium carbonate.

$$CaSO_3 + 3\ C = CaS + 3\ CO.$$
$$CaS + Na_2CO_3 = CaCO_3 + Na_2S.$$

Place the mass on a bright silver coin, and moisten it. A *black stain* will be produced on the silver, due to the formation of silver sulphide, Ag_2S.

$$2\ Ag + Na_2S + H_2O = Ag_2S + 2\ NaOH.$$

If the mass be acidified, sulphuretted hydrogen is given off.

$$Na_2S + 2\ HCl = H_2S + 2\ NaCl.$$

HYDROCHLORIC ACID, HCl.

Solution—Sodium Chloride, NaCl.

1. **Silver nitrate**, $AgNO_3$, gives a *white curdy* precipitate of silver chloride, AgCl: insoluble in strong boiling nitric acid (silver cyanide, AgCN, dissolves): soluble in ammonia.

2. Mix with **manganese dioxide**, MnO_2, and conc. H_2SO_4, and heat: chlorine gas is given off, and may be recognized by its colour, odour, and bleaching action on moist litmus.

$$MnO_2 + 3\ H_2SO_4 + 2\ NaCl = MnSO_4 + 2\ NaHSO_4 + Cl_2 + 2\ H_2O.$$

Note.—Since common MnO_2 frequently contains chlorine (as chloride), a *blank test* should always be made, *i.e.*, some of the MnO_2 should be heated with H_2SO_4 to see whether any chlorine is evolved. If this is the case the sample must be rejected. The best manganese dioxide to use is "needle" or native "manganese."

3. Strong sulphuric acid, when added to a strong solution of a chloride or to the dry salt, produces acid fumes of HCl.

$$H_2SO_4 + NaCl = NaHSO_4 + HCl.$$

CHLORIC ACID, $HClO_3$.

Solution—Potassium Chlorate, $KClO_3$.

1. Heat a small quantity of the dry salt in a test-tube: fusion first takes place, then oxygen is evolved and may be detected by means of a glowing splinter. When action ceases a residue of potassium chloride, KCl, remains. Dissolve this residue in water, and test for HCl by Tests 1, 2, and 3, above.

2. On adding strong H_2SO_4 to a few small crystals of $KClO_3$ in a test-tube, the mixture turns yellow, and a yellowish gas, chlorine peroxide, ClO_2, is evolved. On gently heating, a series of detonations occur.

$$3\,KClO_3 + 2\,H_2SO_4 = 2\,ClO_2 + KClO_4 + 2\,KHSO_4 + H_2O.$$

3. Strong HCl produces a yellow coloration, and a yellow gas is evolved consisting of a mixture of chlorine and chlorine peroxide (called *euchlorine*).

$$8\,KClO_3 + 24\,HCl = 4\,KCl + 6\,H_2O + \underbrace{6\,ClO_2 + 9\,Cl_2}_{\text{Euchlorine}}.$$

4. On charcoal potassium chlorate deflagrates like a nitrate, but more violently.

Note.—Most chlorates are soluble in water; hence the absence of wet tests, which are based on precipitations.

HYDROBROMIC ACID, HBr.

Solution—Potassium Bromide, KBr.

1. Silver nitrate, $AgNO_3$, gives a *yellowish-white* precipitate of silver bromide, AgBr.

$$AgNO_3 + KBr = AgBr + KNO_3.$$

The precipitate is insoluble in dilute nitric acid and almost insoluble in dilute ammonia, but dissolves in strong ammonia. [*Distinction from* HCl.]

2. Add **chlorine water** to the solution: the liquid becomes yellow from free bromine.

$$Cl_2 + 2\,KBr = 2\,KCl + Br_2$$

Shake up with some carbon disulphide, CS_2, which does not mix with the solution, but dissolves out the bromine, and an *orange-coloured* solution of bromine in CS_2 sinks to the bottom.

3. Mix with MnO_2 and H_2SO_4, and heat: bromine vapour of a *reddish-brown* colour is evolved, which colours paper moistened with starch *yellow*. [*Distinction from iodine.*]

$$MnO_2 + 3\,H_2SO_4 + 2\,KBr = MnSO_4 + 2\,KHSO_4 + 2\,H_2O + Br_2.$$

HYDRIODIC ACID, HI.

Solution—Potassium Iodide, KI.

1. **Silver nitrate**, $AgNO_3$, gives a *yellow* precipitate of silver iodide, AgI.

$$AgNO_3 + KI = AgI + KNO_3.$$

The precipitate is insoluble in nitric acid and in dilute ammonia, and is only slightly soluble in strong ammonia, by which, however, it is turned white.

2. **Mercuric chloride**, $HgCl_2$, gives a yellow precipitate, changing to *scarlet*, of mercuric iodide, HgI_2: soluble in excess of $HgCl_2$ or of KI. (See p. 127.)

3. Add a *few drops* of **chlorine water**; the solution becomes *brown* from liberation of iodine.

$$2\,KI + Cl_2 = 2\,KCl + I_2.$$

Shake up with a little CS_2: a fine violet-coloured solution of iodine in CS_2 sinks to the bottom. [*If too much chlorine water is used, colourless* ICl_3 *is formed.*]

4. Mix with MnO_2 and H_2SO_4, and heat in a long test-tube: *violet*-coloured iodine vapour is given off, which condenses in the cool part of the tube in grey-coloured crystals, and turns paper moistened with starch paste *blue*.

$$MnO_2 + 3\ H_2SO_4 + 2\ KI = MnSO_4 + 2\ KHSO_4 + 2\ H_2O + I_2.$$

HYDROFLUORIC ACID, HF.*

Most fluorides are insoluble in water. Those of the alkali metals and silver are, however, soluble. The only important fluorides are fluor spar, calcium fluoride, CaF_2, and cryolite, $3\ NaF, AlF_3$.

Solution—Potassium Fluoride, KF.

1. **Silver nitrate**, $AgNO_3$, gives no precipitate, since silver fluoride, AgF, is soluble in water. [*Distinction from the other halogens.*]

2. **Calcium chloride**, $CaCl_2$, gives a *white gelatinous* pp. of calcium fluoride, CaF_2, difficultly soluble in HCl.

$$CaCl_2 + 2\ KF = CaF_2 + 2\ KCl.$$

3. **Barium chloride**, $BaCl_2$, gives a *white* precipitate of barium fluoride, BaF_2, difficultly soluble in HCl.

$$BaCl_2 + 2\ KF = BaF_2 + 2\ KCl.$$

4. Place some powdered fluor spar in a small leaden trough; add strong H_2SO_4 and mix to a thin paste. Warm gently. Hydrofluoric acid will be freely evolved.

$$H_2SO_4 + CaF_2 = 2\ HF + CaSO_4.$$

Now place a sheet of glass, which has been coated with wax and written on with a sharp point, on the trough, the waxed side being downwards. The writing will be etched on the glass by the action of the fumes of HF on the exposed glass, the silica of the glass being converted into the gas silicon tetrafluoride, SiF_4.

$$SiO_2 + 4\ HF = SiF_4 + 2\ H_2O.$$

* Acids marked with an asterisk are not included in the syllabus but are introduced for the sake of completeness.

5. Mix some powdered fluor spar with some sand, introduce into a test-tube, add strong sulphuric acid, and warm gently. SiF_4 is evolved. Now introduce into the upper part of the tube a glass rod, on the end of which is a drop of water. The SiF_4 and the water react with precipitation of silicic acid, H_2SiO_3, which forms a white film on the rod.

$$3\ SiF_4 + 3\ H_2O = H_2SiO_3 + 2\ H_2SiF_6.$$

NITRIC ACID, HNO_3.

Solution—Potassium Nitrate, KNO_3.

1. Take a weak solution of the nitrate, and dissolve in it a crystal of ferrous sulphate, $FeSO_4$. When quite cold, pour into the tube enough concentrated H_2SO_4 to form a distinct layer at the bottom. A deep *purple* or *brown-coloured* ring will appear where the liquids meet.

The nitrate in the presence of sulphuric acid is reduced to nitric oxide by the ferrous sulphate—

$$6\ FeSO_4 + 4\ H_2SO_4 + 2\ KNO_3 = 3\ Fe_2(SO_4)_3 + K_2SO_4 + 4\ H_2O + 2\ NO.$$

The nitric oxide dissolves in the excess of ferrous sulphate to form the brown compound $(FeSO_4)_2$, NO.

$$2\ FeSO_4 + NO = (FeSO_4)_2,\ NO.$$

Note.—When the addition of $FeSO_4$ produces a precipitate (*e.g.*, with barium nitrate), a portion of the solution should be boiled with sodium carbonate, then filtered, concentrated, and the filtrate acidified with dilute H_2SO_4. The test may then be applied to this solution, which contains the acid as sodium nitrate, the base having been precipitated as a carbonate.

$$FeSO_4 + Na_2CO_3 = FeCO_3 + Na_2SO_4.$$

2. Heat with concentrated sulphuric acid and copper turnings: nitric oxide, NO, is given off, which is converted into brown fumes of nitrogen peroxide, NO_2, in the upper part of the tube, from absorption of oxygen.

$$3\,Cu + 4\,H_2SO_4 + 8\,KNO_3 = 3\,Cu(NO_3)_2 + 4\,K_2SO_4 + 4\,H_2O + 2\,NO.$$
$$2\,NO + O_2 = 2\,NO_2.$$

3. A nitrate heated on charcoal deflagrates.

Note.—All nitrates are soluble in water; hence we have no precipitation reactions. Compare chloric acid.

NITROUS ACID, HNO_2.*

Solution—Potassium Nitrite, KNO_2.

1. On addition of dilute sulphuric acid a brown gas is given off, which consists of a mixture of NO_2 and NO.

$$2\,KNO_2 + H_2SO_4 = K_2SO_4 + NO + NO_2 + H_2O.$$

In the upper part of the tube the NO combines with the oxygen of the air and becomes converted into nitrogen peroxide, NO_2.

[No gas is evolved when nitrates are mixed with dilute sulphuric acid.]

2. A solution of ferrous sulphate gives a *dark brown coloration* on the addition of *dilute* sulphuric acid. [*Distinction from* HNO_3.]

The coloration is due to the formation of the compound $(FeSO_4)_2$, NO.

$$2\,FeSO_4 + 2\,KNO_2 + 2\,H_2SO_4 = Fe_2(SO_4)_2 + K_2SO_4 + 2\,H_2O + 2\,NO.$$
$$2\,FeSO_4 + NO = (FeSO_4)_2,\ NO.$$

In some cases (namely when the solution of the nitrate has an *acid reaction*) the coloration is produced *without* the addition of an acid.

3. A dilute solution of potassium iodide, KI, acidified with H_2SO_4, and to which some starch paste has been added, gives immediately the *blue* iodide of starch.

$$2\,KI + 2\,H_2SO_4 + 2\,KNO_2 = I_2 + 2\,NO + 2\,K_2SO_4 + 2\,H_2O.$$

CARBONIC ACID, H_2CO_3.

1. All carbonates are decomposed by dilute acids with evolution of CO_2. This may be detected by suspending a drop of lime-water on a glass tube over the gas, when the drop soon turns milky.

Distinction between normal and acid carbonates.

1. Acid carbonates or bi-carbonates evolve CO_2 on boiling, and are converted into normal carbonates, *e. g.*,

$$2\,KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

2. Magnesium sulphate, $MgSO_4$, gives no precipitate in the cold with bicarbonates, because $MgH_2(CO_3)_2$ is soluble. On boiling the solution, however, the magnesium bicarbonate is decomposed and a white precipitate of normal carbonate is formed.

$$2\,NaHCO_3 + MgSO_4 = MgH_2(CO_3)_2 + Na_2SO_4.$$
$$MgH_2(CO_3)_2 = MgCO_3 + H_2O + CO_2.$$

Normal carbonates give a precipitate of $MgCO_3$ at once.

$$Na_2CO_3 + MgSO_4 = MgCO_3 + Na_2SO_4.$$

BORIC ACID, H_3BO_3.*

Solution—Borax, $Na_2B_4O_7$.

1. Add HCl to a solution of borax; wet a piece of turmeric paper with the solution. The paper when dried

becomes reddish-brown, and, on treating with *dilute* caustic soda, changes to a purplish blue-black.

Dry the paper by coiling round the exterior of a test-tube, partially filled with water, and boiling the water in the tube over the Bunsen flame.

2. Place a small quantity of the dry salt in a porcelain dish, and make into a paste with H_2SO_4; cover with alcohol, and ignite: the alcohol burns with a *green flame*, due to the liberated boric acid.

$$Na_2B_4O_7 + H_2SO_4 + 5\ H_2O = 4\ H_3BO_3 + Na_2SO_4.$$

3. Place a small quantity of the dry salt on the loop of the platinum-wire, and heat in the Bunsen flame. The borate at once swells up, and then shrinks and fuses to a transparent glass, consisting of anhydrous borax. If the salt is moistened with HCl or H_2SO_4 before heating, and held just at the *edge* of the flame, the flame is tinged *green*, due to the free boric acid.

SILICIC ACID, H_2SiO_3.*

Solution—Sodium Silicate, Na_2SiO_3.

1. Add HCl, and evaporate in an evaporating dish to dryness; when cold, moisten with HCl, heat, and add water: white flakes of silica, SiO_2, will remain undissolved.

$$2\ HCl + Na_2SiO_3 = H_2SiO_3 + 2\ NaCl.$$
$$H_2SiO_3 = H_2O + SiO_2.$$

The silicic acid first formed as in the first equation loses water when the evaporation is carried to dryness as represented in the second equation.

2. Fuse a colourless silicate in a bead of microcosmic salt: the silica floats about in the bead as a skeleton.

PHOSPHORIC ACID, H_3PO_4.*

Solution—Sodium Phosphate, Na_2HPO_4.

1. **Silver nitrate,** $AgNO_3$, gives a *yellow* precipitate of silver phosphate, Ag_3PO_4, soluble in NH_4OH and in acids.

$$3\,AgNO_3 + Na_2HPO_4 = Ag_3PO_4 + 2\,NaNO_3 + HNO_3.$$

2. **Ammonium chloride,** NH_4Cl, **ammonium hydroxide,** NH_4OH, and **magnesium sulphate,** $MgSO_4$, give a *white crystalline* precipitate of ammonium magnesium phosphate, NH_4MgPO_4.

$$2\,NH_4Cl + NH_4OH + MgSO_4 + Na_2HPO_4 = MgNH_4PO_4 + (NH_4)_2SO_4 + 2\,NaCl + H_2O.$$

Precipitation is favoured in dilute solutions by agitation and allowing to stand for a time.

3. **Ammonium molybdate,** $(NH_4)_2MoO_4$, gives, on gently warming, a *finely divided yellow* precipitate in solutions containing excess of nitric acid. The precipitate probably has the composition $(NH_4)_3PO_4$, $12\,MoO_3$. In dilute solutions the liquid becomes yellow, but a precipitate is formed only after gentle warming and standing for some hours. The solution must not be too strong in phosphate.

4. **Barium chloride,** $BaCl_2$, gives a *white* precipitate of $Ba_3(PO_4)_2$, soluble in dilute acids. If the solution is neutralized by adding ammonia, $Ba_3(PO_4)_2$ is reprecipitated.

$$3\,BaCl_2 + 2\,Na_2HPO_4 = Ba_3(PO_4)_2 + 4\,NaCl + 2\,HCl.$$

$$Ba_3(PO_4)_2 + 6\,HCl + 3\,BaCl_2 + 2\,H_3PO_4.$$

$$3\,BaCl_2 + 2\,H_3PO_4 + 6\,NH_4OH = Ba_3(PO_4)_2 + 6\,NH_4Cl + 6\,H_2O.$$

5. **Ferric chloride** gives a *yellowish-white* precipitate of ferric phosphate, $FePO_4$.

$$FeCl_3 + Na_2HPO_4 = FePO_4 + 2\,NaCl + HCl.$$

The precipitate is soluble in dilute mineral acids but *insoluble in acetic acid.*

ARSENIC ACID, H_3AsO_4.*

Solution—Sodium Arsenate, Na_2HAsO_4.

1. **Silver nitrate**, $AgNO_3$, gives a *brick-red* precipitate of silver arsenate, Ag_3AsO_4. [*Distinction from phosphoric acid.*]

$$3\ AgNO_3 + Na_2HAsO_4 = Ag_3AsO_4 + 2\ NaNO_3 + HNO_3.$$

The precipitate is soluble in ammonia and in nitric acid.

2. **Ammonium chloride**, NH_4Cl, **ammonium hydroxide**, NH_4OH, and **magnesium sulphate**, $MgSO_4$, produce a *white crystalline* precipitate of NH_4MgAsO_4, similar in appearance and properties to NH_4MgPO_4.

$$Na_2HAsO_4 + 2\ NH_4Cl + NH_4OH + MgSO_4 = (NH_4)MgPO_4 + 2\ NaCl + (NH_4)_2SO_4 + H_2O.$$

[The corresponding arsen*ious* compound, $(NH_4)MgAsO_3$, is soluble in water, so no precipitate is formed when an arsen*ite* is treated with $MgSO_4 + NH_4Cl + NH_4OH$.]

3. **Ammonium molybdate**, $(NH_4)_2MoO_4$, in excess gives, on boiling, a *yellow* precipitate, having the composition $(NH_4)_3AsO_4$, $12\ MoO_3$, in solutions made strongly acid with nitric acid.

4. Add concentrated hydrochloric acid ; heat to boiling, and pass H_2S. A *yellow* precipitate of arsenious sulphide, As_2S_3, mixed with sulphur, is obtained. [*Difference from phosphate.*]

$$2\ Na_2HAsO_4 + 4\ HCl + 5\ H_2S = As_2S_3 + S_2 + 4\ NaCl + 8\ H_2O.$$

The reduction proceeds much more quickly if sulphurous acid be added before passing H_2S.

5. **Ferric chloride**, $FeCl_3$, gives a white precipitate of ferric arsenate, $FeAsO_4$.

$$FeCl_3 + Na_2HAsO_4 = FeAsO_4 + 2\,NaCl + HCl.$$

The precipitate is soluble in dilute mineral acids, but *insoluble in acetic acid.*

6. **Copper sulphate**, $CuSO_4$, gives a *light blue* precipitate of cupric hydrogen arsenate, $CuHAsO_4$.

$$CuSO_4 + Na_2HAsO_4 = CuHAsO_4 + Na_2SO_4.$$

ARSENIOUS ACID, H_3AsO_3.

Solution—Arsenious Oxide, As_4O_6, dissolved in Hydrochloric Acid, HCl.

[*See Arsenic, page* 136.]

CHROMIC ACID, H_2CrO_4.*

Solution—Potassium Chromate, K_2CrO_4.

(All chromates are red or yellow.)

1. **Silver nitrate**, $AgNO_3$, gives a *dark red* precipitate of silver chromate, Ag_2CrO_4. (See p. 120.)

2. On adding **dilute sulphuric acid**, the colour of the solution darkens, owing to formation of chromic acid, H_2CrO_4. To this solution add sulphurous acid: the solution becomes *green* from reduction, thus:—

$$2\,H_2CrO_4 + 3\,H_2SO_3 = Cr_2(SO_4)_3 + 5\,H_2O.$$

3. **Lead acetate** gives a *yellow* precipitate of lead chromate, $PbCrO_4$. (See p. 122.)

4. On passing a current of H_2S gas through an acid solution of a chromate, reduction takes place; the solution becomes green owing to the formation of chromic chloride, $CrCl_3$ (if HCl is the acid used), and sulphur is precipitated. Thus—

$$2\ K_2CrO_4 + 3\ H_2S + 10\ HCl = 4\ KCl + CrCl_3 + 8\ H_2O + S.$$

Note.—This reaction should be carefully noted, as it is likely to cause some perplexity in testing for the metals of Group II.

PERMANGANIC ACID, $HMnO_4$.*

(Commonest permanganates, $KMnO_4$, $NaMnO_4$.)

Solution—Potassium Permanganate, $KMnO_4$.

1. The purple colour of permanganate solutions is distinctive.

2. **Silver nitrate,** $AgNO_3$, gives a *dark red* precipitate of $AgMnO_4$.

$$KMnO_4 + AgNO_3 = AgMnO_4 + KNO_3.$$

3. **Sulphurous acid,** H_2SO_3, decolorizes the solution, the sulphurous acid being oxidized to sulphuric acid.

$$2\ KMnO_4 + 5\ H_2SO_3 = 2\ KHSO_4 + 2\ MnSO_4 + H_2SO_4 + 3\ H_2O.$$

4. An acid solution is also decolorized by **ferrous sulphate** solution, the ferrous sulphate being converted into ferric sulphate, $Fe_2(SO_4)_3$

$$2\ KMnO_4 + 8\ H_2SO_4 + 10\ FeSO_4 = 5\ Fe_2(SO_4)_3 + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O.$$

5. **Sulphuretted hydrogen,** H_2S, decolorizes an acid solution of a permanganate, sulphur being precipitated. For this reason a permanganate is decolorized in Group II.

$$2\ KMnO_4 + 5\ H_2S + 3\ H_2SO_4 = 2\ MnSO_4 + K_2SO_4 + 8\ H_2O + 5\ S.$$

TABLE OF SOLUBILITIES.

TABLE SHOWING THE SOLUBILITY OF THE MORE COMMONLY OCCURRING SALTS.

NAME.	SOLUBLE IN WATER.	SOLUBLE IN, OR DECOMPOSED BY, ACIDS.	INSOLUBLE IN ACIDS.
Carbonates.	Acid carbonates of Ba, Sr, Pb, Mn, Mg, Fe″, and Ca, and alkaline carbonates.	All carbonates are decomposed with evolution of CO_2.	
Sulphates.	Most sulphates. (Ag_2SO_4 is difficultly soluble).	Some *basic* sulphates.	Sulphates of Pb, Ba, Sr and Ca, and red chromic sulphate.
Nitrates.	Most nitrates (a few *basic* nitrates excepted).	A few basic nitrates which are readily soluble in dilute HNO_3.	
Chlorides.	Most chlorides.	A few oxychlorides. (BiOCl and SbOCl).	Chlorides of Pb, Hg′, Ag, and Cu_2Cl_2.
Bromides.	Most bromides.	Cu_2Br_2 in HCl.	Bromides of Hg′, Ag, and Pb.
Iodides.	Most iodides.	HgI_2, Hg_2I_2 ($=HgI_2+Hg$), PbI_2, Cu_2I_2, decomposed by HNO_3 with evolution of I.	Iodides of Ag, Hg′, Hg″, Pb, and 'Cu'.
Chlorates.	All chlorates.		
Sulphides.	Sulphides of the alkali metals, and the metals of the alkaline earths. MgS and CaS *very slightly* soluble.	All other sulphides are decomposed by HCl (H_2S being evolved), or by HNO_3, or aqua regia, with separation of S.	
Phosphates.	Alkaline phosphates only.	Remainder are soluble.	
Chromates.	Alkaline chromates and chromates of Mg, Zn, Ca, Sr, Fe^{iv}, and Cu.	Chromates insoluble in water dissolve in acids (evolving chlorine in concentrated HCl).	Ignited lead chromate.

CHAPTER IV.

SYSTEMATIC ANALYSIS OF SALTS.

Preliminary Examination in the Dry Way.

If the substance is in solution, a portion should be evaporated to dryness on a water-bath while the examination in the wet way is being proceeded with. The residue after evaporation should then be examined as below, I–IX.

I. Note the general physical characteristics of the substance.

On this point the previous experience of the student must be his guide. He should note the appearance, colour, lustre, crystalline form, etc., of all substances with clearly marked characteristics which come under his notice. It is useless to give any list of such substances, as they must be seen to be recognized.

II. Heat a small portion of the powdered substance in a bulb-tube in the Bunsen flame.

Observation.	Inference.
1. *The substance fuses and solidifies on cooling.*	Salts of the alkalies or alkaline earths.
2. *The substance changes colour—*	

Observation.	Inference.
(*a*) *Yellow* while *hot*, *white* on *cooling*.	ZnO, Sb_4O_6.
(*b*) From *white* to *yellowish-brown* when *hot*, *dirty light yellow* on *cooling*.	SnO_2.
(*c*) *Dark red* while *hot*, *yellowish-brown* on *cooling*.	Fe_2O_3.
(*d*) From *white* to *orange* and *reddish-brown*, *dull yellow* on cooling, fusible at an intense heat.	Bi_2O_3.
(*e*) From *yellow* to *reddish-brown* while *hot*, *yellow* when *cold*, fusible at a red heat.	PbO.
3. *The substance gives off water with or without fusion.*	Salts containing water of crystallization; also *acid* salts (*e.g.* $NaHCO_3$)
4. *The substance first swells up and then shrinks.*	Alums, phosphates, borates.
5. *The substance volatilizes and condenses as a sublimate in the upper part of the tube*—	S, Hg, As, Sb, NH_4.
(*a*) *Reddish* drops, *yellow* when *cold*.	Sulphur or a sulphide.
(*b*) *Black* sublimate, which becomes *red* on rubbing.	HgS.
(*c*) *Yellow* sublimate.	As_2S_3, HgI_2.
(*d*) Sublimate of *small white octahedral crystals*.	As_4O_6.
6. *A gas is evolved*—	
(*a*) O (test with glowing splinter).	Chlorates, nitrates, peroxides.

Observation.	Inference.
(*b*) Brown fumes of $\dot{N}O_2$.	Nitrates of heavy metals, Pb, Bi, Hg, etc.
(*c*) NH_3 (smell and alkaline reaction).	Salts of NH_4, combined with a *non-volatile acid.*
(*d*) Violet vapours of iodine.	Iodides.
(*e*) CO_2 (lime-water test).	Carbonates (except those of the alkalies).
(*f*) Cl (bleaching action, smell and colour).	Hypochlorites and some chlorides and chlorates.
(*g*) Br (smell and colour).	Some bromides and bromates.
(*h*) SO_2 (smell).	Sulphites, sulphur compounds.

III. **Heat a portion of the substance on charcoal in the outer blowpipe flame.**

1. *It decrepitates.*	NaCl, KI, etc.
2. *It fuses and sinks into the charcoal.*	Alkaline salts.
3. *It deflagrates.*	Chlorates, nitrates and certain oxides.
4. *A white mass remains, highly luminous while heated.*	Alkaline earths, Al_2O_3, SiO_2, ZnO, SnO_2.
5. *A coloured residue is left on the charcoal.*	Cu, Co, Ni, Mn, Fe, Cr.
6. *White fumes are given off.*	Hg, As, Sb, and NH_4 compounds.

OBSERVATION.	INFERENCE.
7. *An incrustation is formed on the charcoal—*	
(*a*) *White* incrustation.	NH_4, Hg, Sb, Zn.
(*b*) *White* (with garlic odour).	As.
(*c*) *Yellow* when *hot*, *white* when *cold*.	Zn.
(*d*) *Reddish-brown.*	Cd.
(*e*) *Straw colour.*	Sn.
(*f*) *Brown* when *hot*, *yellow* when *cold*.	Pb.
(*g*) *Brown* when *hot*, *orange* when *cold*.	Bi.

IV. Moisten the cold residue of III. (if white) with cobalt nitrate, $Co(NO_3)_2$ and heat strongly.

1. *The residue is coloured—*	
Blue.	Al_2O_3, phosphates, borates and silicates.
Pale pink (colour indistinct).	MgO.
Green.	ZnO.
Bluish-green (dirty).	Sn.

V. Mix a portion of the substance carefully with fusion mixture and a trace of KCN, and heat on charcoal in the inner blowpipe flame.

1. *A metallic bead is obtained.*	
(*a*) A white malleable bead which marks paper (*yellow incrustation* on charcoal).	Pb.
(*b*) Soft, white malleable bead (*slight yellowish incrustation*).	Sn.

Observation.	Inference.
(*c*) Hard white malleable bead (*no incrustation*).	Ag.
(*d*) White brittle bead (*yellow incrustation*).	Bi.
(*e*) White brittle bead (*white fumes* and *incrustation*).	Sb.
2. *Red infusible scales.*	Cu.
3. *Magnetic metallic particles.*	Fe, Ni, Co.
4. *When the fused mass is placed on a bright silver coin and moistened with a drop of water, a black stain of* Ag_2S *is produced.*	Sulphur compounds.

VI. Hold a piece of the substance moistened with HCl on the loop of a CLEAN platinum wire in the Bunsen flame.

1. The flame is *yellow*,	Na.
2. ,, ,, *violet*,	K.
3. ,, ,, *intense crimson*,	Sr.
4. ,, ,, *yellowish-green*,	Ba.
5. ,, ,, *orange-red*,	Ca.
6. ,, ,, *green*,	H_3BO_3, or Cu.
7. ,, ,, *blue*,	Pb, Bi, $CuCl_2$, As_4O_6.

It is almost impossible to distinguish from one another by the eye, the colours given to the flame by Pb, Bi, As, Sb, and K. Arsenic compounds always evolve a visible white fume, and lead invariably corrodes the platinum.

VII. If the substance is coloured, heat on borax bead.

Observation.		Inference.
Oxidizing Flame.	*Reducing Flame.*	
Green.	Green.	Cr.
Yellow (cold), brown (hot)	Dirty green, olive.	Fe.
Amethyst.	Colourless.	Mn.
Violet (hot) to yellow-brown (cold).	Grey and opaque.	Ni.
Blue.	Blue.	Co.
Green (hot), blue (cold).	Colourless or red.	Cu.
Black (too much of the substance has been used).		

VIII. Heat a small quantity of the substance in a test-tube with a little dilute HCl.

Observation.	Inference.
A gas is evolved—	
(*a*) CO_2 (lime-water test).	Carbonates.
(*b*) H_2S (smell, and lead acetate paper test).	Sulphides, except those of the metals of Groups I. and II.
(*c*) SO_2 (smell of burning sulphur).	H_2SO_3.
(*d*) SO_2 and separation of yellow sulphur.	$H_2S_2O_3$.
(*e*) Cl (smell, and bleaching test).	HClO or oxidizing agents, *e.g.*, chromates, chlorates, etc.
(*f*) NO_2 (colour and smell).	Nitrite.
2. Smell like that of vinegar.	Acetate.

IX. **Heat in a test-tube with concentrated sulphuric acid:—**

Observation.	Inference.
1. *Gas is evolved*—	
(*a*) HCl (smell and white fumes* with ammonia).	Chloride.
(*b*) HF (oily appearance in the tube).	Fuoride.
(*c*) I (violet vapours).	Iodide.
(*d*) Br (smell and colour and action on starch paper).	Bromide.
(*e*) NO_2 (smell and colour).	Nitrite or nitrate.
(*f*) ClO_2 (smell, colour and crackling).	Chlorate.

EXAMINATION FOR BASE.

Preparation of Solution.

1. If the substance is solid, it should be finely powdered; then try if it is soluble in water, in the cold or on boiling. If insoluble in water, try first dilute HCl, then concentrated HCl. If insoluble in HCl, try aqua regia.

Note.—It will generally be found unnecessary to employ aqua regia, but, if used, the solution should be evaporated to dryness with excess of HCl, and the residue dissolved in warm water before proceeding with the examination.

* A number of other acids also give white fumes with ammonia, *e.g.*, HNO_3, HF, HBr.

2. If the substance is insoluble in the above solvents, powder it very finely and mix thoroughly with five or six times its weight of pure fusion mixture. Heat the mixture on a boat made of a large piece of platinum-foil, first over the Bunsen flame, and then over the blowpipe. When cold, boil the foil and the fused mass with water until the whole mass is completely broken up and separated from the foil. The *solution* now contains the *acid* of the substance combined with K and Na, while the *residue* contains the *base* as an oxide or carbonate. Filter off and wash the residue with hot water until the washings give no alkaline reaction. Then—

(*a*) Test *filtrate* for *acid*, as directed in examination for acids.

(*b*) Test residue for base by dissolving in dilute HCl and proceeding as detailed below.

Note.—The most commonly occurring insoluble substances are—native or ignited alumina and chromic oxide; silica and many silicates; barium, strontium and lead sulphates; silver chloride, cyanide, bromide, and iodide; many minerals, *e.g.*, chrome iron ore, calcium fluoride; carbon and sulphur.

3. If the substance is provided in solution, or is soluble in water, test with litmus paper. If the reaction is—

(*a*) *Acid.* Free acid, acid salt, or a normal salt having an acid reaction, may be present.

(*b*) *Alkaline.* Free alkali, or alkaline earth, or a sulphide of an alkali, or a strong alkali (*e.g.*, KOH or NaOH united with a weak acid—*e.g.*, H_2CO_3, H_3PO_4, etc.), may be present.

(*c*) *Neutral.* Water, or one or more of a large number of salts, may be present.

When the solution is prepared, the examination must be carried on in accordance with the following tables. When the metal is found by this method, its presence should be confirmed by the special tests given in Chapter II.

TABLE A.

GENERAL TABLE FOR THE ANALYSIS OF A SUBSTANCE CONTAINING ONLY ONE BASE.

To a portion of the solution add **HCl**.

Pp., if produced, may be—

Ag Cl (*white*).
Hg$'_2$Cl$_2$ (*white*).
Pb Cl$_2$ (*white*).

If pp. is produced, continue analysis by Table I.

Note I.—If solution is dilute, Pb may not be precipitated in this group.

Note II.—Do not confound the precipitate of the oxychlorides of Antimony and Bismuth (see p. 139, 2 and p. 128, 2) with that of these chlorides.

If no pp. is produced, to the *same* portion of the solution add **H$_2$S** water.
If a pp. is indicated, pass a current of **H$_2$S** gas through the solution.

Pp., if produced, may be—

Insoluble in NaHO or (NH$_4$)$_2$S + S:
Hg S (*black*)
Pb S (*black*)
Bi$_2$S$_3$ (*black*)
Cu S (*black*)
Cd* S (*yellow*)

Soluble in NaHO or (NH$_4$)$_2$S + S:
Sn S (*brown* or *black*)
Sn S$_2$ (*yellow*)
As$_2$S$_3$ (*yellow*)
Sb$_2$S$_3$ (*orange*)

If pp. is produced, continue analysis by Table II.

*Before passing on to next group, dilute the solution considerably with water, and gently warm; Cd may then be precipitated. The presence of much HCl prevents the precipitation of CdS.

If no pp. is produced, to a fresh portion of the solution add **NH$_4$Cl** and **NH$_4$OH** in excess after boiling with a *few drops* of HNO$_3$ to oxidize Fe″, if present, to Fe‴. (See page 140.)

Pp., if produced, may be—

Fe(OH)$_3$ (*reddish-brown*).
Cr(OH)$_3$ (*darkish-green*).
Al(OH)$_3$ (*white*).

If pp. is produced, continue analysis by Table III.

A **phosphate** of any of the metals of Groups III., IV., and V., or Mg, might be precipitated by NH$_4$Cl and NH$_4$OH.

Mn, if present, is also partially precipitated in this group. See Note to Table III.

If no pp. is produced, to the same portion of the solution add **(NH$_4$)$_2$S**.

Pp., if produced, may be—

Ni S (*black*).
Co S (*black*).
Mn S (*buff*).
Zn S (*white*).

If pp. is produced, continue analysis by Table IV.

If no pp. is produced, to a fresh portion of the solution add **NH$_4$Cl**, **NH$_4$OH** in excess, and **(NH$_4$)$_2$CO$_3$**.

Pp., if produced, may be—

Ba CO$_3$ (*white*).
Sr CO$_3$ (*white*).
Ca CO$_3$ (*white*).

If pp. is produced, continue analysis by Table V.

If no pp. is produced by above reagents, metal must be either **Mg**, **NH$_4$**, **Na**, or **K**.

Continue analysis by Table VI.

TABLE I.

<table>
<tr><td colspan="3">Examination for the Metals of Group I.</td></tr>
<tr><td colspan="3">Shake up the pp., allow to subside, and pour off the clear liquid. To the residue add an excess of NH_4OH.</td></tr>
<tr><td>The pp. dissolves and is reprecipitated on addition of HNO_3 in excess.

Presence of
Ag.</td><td>The pp. is blackened.

Presence of
Hg′
(mercurous).</td><td>The pp. is not affected by NH_4HO.

Presence of Pb.

Confirm by precipitating a fresh portion of the solution with HCl. On boiling, the pp. should dissolve.</td></tr>
<tr><td colspan="3">Confirm by special tests on pp. 120 to 125.</td></tr>
</table>

TABLE II.

Examination for the Metals of Group II.

Filter and wash pp. on filter until free from HCl and H_2S, then gently warm a portion of the pp. with NaOH, or $(NH_4)_2S + S$.

<table>
<tr><td colspan="4">The pp. does not dissolve.</td><td colspan="3">The pp. dissolves. Heat another portion of the pp. with $(NH_4)_2CO_3$.</td></tr>
<tr><td colspan="3">The pp. is black.
Boil a fresh portion of it with HNO_3.</td><td rowspan="2">A yellow pp. indicates presence of Cd.</td><td rowspan="2">The yellow pp. dissolves.

Presence of As.</td><td colspan="2">The pp. does not dissolve.</td></tr>
<tr><td rowspan="2">The black pp. does not redissolve, but may be converted into a white compound of Hg.

Presence of Hg (mercuric).</td><td colspan="3">The pp. dissolves. To separate portions of the original solution add—</td><td>An orange pp. indicates presence of Sb.</td><td>A brown or yellow pp. indicates presence of Sn,
Stannous (brown),
Stannic (yellow).</td></tr>
<tr><td>A little dilute H_2SO_4.

A white pp. indicates formation of $PbSO_4$.
Presence of Pb.</td><td>A little NH_4Cl and an excess of water.

A white pp. indicates presence of Bi.</td><td>NH_4OH in excess.

A blue solution indicates presence of Cu.</td><td colspan="3"></td></tr>
</table>

Confirm by special tests on pp. 126 to 140.

TABLE III.

Examination for the Metals in Group III.		
The pp. is		
Reddish-brown.	*Green.*	*White gelatinous.*
Presence of **Fe.**	Presence of **Cr.**	Presence of **Al.**
Test original solution for Fe″ or Fe‴ by $K_4Fe_6(CN)_6$, $K_3Fe(CN)_6$, and KCNS + $HgCl_2$.		
Confirm by special tests on pp. 140 to 145.		

Note.—Manganese, if present, is usually partially pptd. in this group. *Manganous* hydroxide is white, and its formation is prevented by the presence of ammonium chloride (hence use of this reagent in Group III.), but, on exposure to air, the solution absorbs oxygen and a hydrated *manganic* oxide, $Mn_2O_2(OH)_2 = Mn_2O_3$, H_2O is slowly thrown down in the form of a brown precipitate. If, therefore, the solution, after addition of NH_4Cl and NH_4OH, remains clear for a short time, and then a pp. of a dark brown colour begins to form, manganese may be suspected, and the addition of $(NH_4)_2S$ to the turbid liquid will produce the buff-coloured pp. of **MnS.**

TABLE IV.

Examination for the Metals of Group IV.			
The pp. is			
Black. To a portion of the original solution add NaOH.		*Buff* or *flesh-coloured.*	*White.*
An *apple-green* pp. indicates presence of **Ni.**	A *bluish-white* pp. indicates presence of **Co.**	Presence of **Mn.**	Presence of **Zn.**
Ni and **Co** are readily detected in the Preliminary examination by the bead test.			
Confirm by special tests on pp. 145 to 151.			

TABLE V.

Examination for the Metals of Group V.

To a portion of the solution, which must not be too acid, add $CaSO_4$.

A *white* pp., produced *immediately*, indicates presence of **Ba.**	A *white* pp., produced *after* gently warming and stirring the solution for *some time*, indicates presence of **Sr.**	*No* pp. indicates presence of **Ca.** Confirm by adding $Am_2C_2O_4$ to a fresh portion of original solution. A *white* pp. of CaC_2O_4 is obtained.
Ba and **Sr** are readily detected in the Preliminary examination by the flame test.		

Confirm by special tests on pp. 152 to 155.

TABLE VI.

Examination for the Metals of Group VI.	
Heat a portion of original substance (dry, or in solution, better dry) with NaOH or $Ca(OH)_2$ in a test tube. Evolution of NH_3 indicates presence of ...	**NH_4.**
To a portion of original solution add NH_4Cl, NH_4OH, and Na_2HPO_4, and stir with a glass rod. A *white crystalline* pp. of $MgAmPO_4$ indicates presence of	**Mg.**
Evaporate another portion of solution to dryness. Heat to expel ammonium salts, take up a portion of residue with water, and add (on a watch-glass, see page 156) a few drops of $PtCl_4$. A *yellow crystalline* pp. of K_2PtCl_6 indicates presence of	**K**
To another portion of the residue apply flame test. Intense *golden yellow flame* indicates presence of	**Na.**

EXAMINATION FOR ACID.

In testing for acids, the student should be guided by—

(*a*) *The results of the preliminary examination.* In many cases the acid will have been detected in this examination, and it is only necessary to confirm the result in the wet way.

(*b*) *The result of the examination for the base.* The base being now known, and the properties and solubility of the substance being determined, the field of search is often considerably narrowed. If no acid is found, the substance may be an oxide or hydroxide, and here again a knowledge of the nature of the base helps to decide whether such a compound is likely to occur.

A knowledge of the commoner compounds of each metal is often suggestive, but should not encourage random shots.

Preparation of Solution.

1. *The substance is in solution or soluble in water.*

If metals of Groups I. or II. be present, remove them by boiling with a slight excess of pure sodium carbonate, filter, and use the filtrate for the examination for acids. If Groups I. and II. be absent, use the original solution.

2. *The substance is insoluble in water, but soluble in acids.*

Boil a portion of the solid with a strong solution of sodium carbonate, filter, and use the filtrate.

3. *The substance is insoluble.*

Treat as described for the preparation of the solution for the examination for bases, using the aqueous filtrate.

Before adding the reagents, exactly neutralize a portion of the solution with HNO_3, or, if acid, with ammonia. If the solution has been boiled with sodium carbonate, the liquid will be strongly alkaline. In this case, make it distinctly acid with HNO_3, boil to expel CO_2, and then neutralize back again with ammonia.

Test and Observation.	Inference.
1. *To neutral solution add* $BaCl_2$.	
White pp., *insoluble* in HCl.	Presence of H_2SO_4 (or H_2SiF_6).
White pp., *soluble* in HCl.	H_3PO_4, H_2SO_3, H_3BO_3, H_2SiO_3, $H_2S_2O_3$, (pp. dissolves, but S is slowly thrown down), H_2CO_3 (pp. dissolves with effervescence).
Yellow pp.	H_2CrO_4.
2. *To another portion add* $AgNO_3$.	
(*a*) A pp. *soluble* in HNO_3.	
i. White, soluble in ammonia.	HNO_2, H_2CO_3, H_2SiO_3 H_3BO_3.
ii. Yellow.	H_3PO_4, H_3AsO_3.
iii. Red.	H_3AsO_4.
iv. Dark red.	H_2CrO_4
(*b*) A pp. *insoluble* in HNO_3.	
i. White, soluble in ammonia.	HCl, HCN, HClO.
ii. Yellowish white, soluble in ammonia.	HBr.
iii. Yellow, insoluble in ammonia.	HI.
iv. Black, ditto.	H_2S.
v. Orange-red, soluble in ammonia.	$H_3Fe(CN)_6$.
vi. White, insoluble in ammonia.	$H_4Fe(CN)_6$.
vii. White, turning yellow, dark brown, and finally black.	$H_2S_2O_3$.

Test and Observation.	Inference.
If no pp. is produced by $BaCl_2$ or $AgNO_3$—	
3. *To a portion of solution add a solution of* $FeSO_4$, *and then pour down the side of the test-tube strong* H_2SO_4. See Note, p. 167.	
A *brown ring* formed at junction of fluids indicates	HNO_3.
4. *Heat a small portion of dry substance (or residue after evaporation) in a test-tube with conc.* H_2SO_4.	
Evolution of ClO_2 and detonation indicates	$HClO_3$.
If no acid is detected by 1, 2, 3, or 4.	
5. *To a fresh portion of the solution add* $FeCl_3$.	
A *red coloration*, not destroyed on boiling, but destroyed by addition of $HgCl_2$, indicates	HCNS.
Deep green or brown coloration indicates	$H_3Fe(CN)_6$.
Deep blue pp. indicates	$H_4Fe(CN)_6$.

[H_3AsO_3 and $HAsO_2$ will have been detected in the examination for the base.]

Free Acids.

[Only HCl, HNO_3, and H_2SO_4 are considered here.]

If you are given a solution and find on going through the groups that no base is present, proceed as follows :—

(1) Test with blue litmus, which will be turned red.

(2) Evaporate a portion of the solution to dryness. Intensely acid fumes are given off and no residue remains.

(3) Neutralise the other portion of the solution with NaOH, and test for the acid in the ordinary way.

Hydroxides.

If, on the other hand, the solution contains a metal, but no acid radicle, then the metal must be present as the hydroxide. [Also since the only soluble hydroxides are those of K, Na, NH_4, Ba, Sr, Ca, Mg (slightly), only these metals can be present.] The solution will then answer to the following tests :—

1. Silver nitrate gives a brown precipitate of silver oxide, Ag_2O, soluble in ammonia. (See p. 121.)

2. Mercuric chloride gives a yellow precipitate of mercuric oxide, insoluble in excess. In the case of ammonia, the precipitate is white, consisting of mercurammonium chloride, $HgNH_2Cl$. (See p. 127.)

3. The solution is strongly alkaline.

1. White, crystalline. Soluble in water. Neutral.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in a dry bulb-tube.	Brown nitrogen peroxide evolved.	Nitrate of heavy metals.
,, with HCl.	White insoluble substance formed on addition of acid; dissolves on heating.	[Grp. I. (Pb)]
,, ,, H_2SO_4.	Oxides of N.	HNO_3.
,, ,, Na_2CO_3.	Deflagrates: metallic malleable bead which marks paper; blue flame.	Pb.
,, on platinum wire.	Blue flame.	Pb, As, Sb.

Wet Examination for Base.

Added HCl.	White pp.: dissolves on boiling: H_2S added to solution thus obtained: *reddish-brown* and finally black pp. is obtained.	Pb.
,, KI.	Yellow pp.	,,
,, K_2CrO_4.	,,	,,

Examination for Acid.

Boiled with Na_2CO_3 to remove Pb, neutralized with HNO_3, and added $BaCl_2$.	No pp.	—
Added $AgNO_3$.	,,	—
Pptd Pb from sol. with Na_2CO_3, filtered, acidified with H_2SO_4, and added $FeSO_4$, and H_2SO_4.	Brown ring formed.	HNO_3.

$FeSO_4$ pptates. Pb as $PbSO_4$. See p.167, Note.

Base, PbO. **[Lead Nitrate, $Pb(NO_3)_2$.]** **Acid, HNO_3.**

2. White crystalline substance. Soluble in water.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in a dry tube.	Sublimes, gives off water and brown fumes.	Nitrate of a heavy metal.
Mixed a portion with Na_2CO_3 and KCN, and heated in a dry tube.	A mirror forms on upper part of tube; globules are obtained on rubbing with a roll of filter paper.	Mercury.
Heated with HCl.	[A white pp. formed.]	
,, ,, H_2SO_4.	Oxides of N given off.	A nitrate.

Wet Examination for Base.

Added HCl.	A white pp.	Hg′, Ag, or Pb.
Washed pp. with hot water.	The pp. insoluble.	
Added NH_4OH to pp.	,, ,, is blackened.	**Hg′.**

Examination for Acid.

Tested for HNO_3 by adding H_2SO_4 and $FeSO_4$.	A brown ring formed.	**HNO_3.**

Base, Hg_2O. **Acid, HNO_3.**

[Mercurous Nitrate, $Hg_2(NO_3)_2$.]

3. White, crystalline. Soluble in a very small amount of water, and giving milky-white precipitate with excess of water.

PRELIMINARY EXAMINATION.

Experiment.	*Observation.*	*Inference.*
Heated in dry bulb-tube.	Brown nitrogen peroxide evolved.	Nitrate of heavy metal.
,, with HCl.		
,, ,, H_2SO_4.	Nitrogen peroxide evolved.	HNO_3.
,, on charcoal with Na_2CO_3.	Brittle metallic beads, with orange-yellow incrustation.	Bi.
,, with platinum wire.	Blue flame.	Pb, As, Sb, Bi.

WET EXAMINATION FOR BASE.

Added HCl.	Milky-white pp. dissolving in excess of HCl.	Absence of Grp. I. Probably Sb or Bi present.
,, H_2S.	Brownish-black pp.	Hg, Pb, Bi, Cu, Sn.
Treated pp. with $(NH_4)_2S$.	Insoluble.	Hg, Pb, Bi, Cu.
Boiled pp. with strong HNO_3 and a few drops of dilute H_2SO_4.	Soluble.	Bi.
Add nitric acid. Boil. Pp. dissolves.		
Add H_2SO_4. No pp. shows Pb is absent.		

EXAMINATION FOR ACID.

Preliminary examination conclusively shows presence of nitric acid.

Base, Bi_2O_3. **Acid, HNO_3.**

[Bismuth Nitrate, $Bi(NO_3)_3$.]

4. White Crystalline Substance. Soluble in Water. Neutral.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in dry bulb tube.	Water of crystallization evolved. Residue yellow to brown when hot.	Pb, Zn, Cd.
,, with HCl.	——	——
,, ,, H_2SO_4.	Brown fumes (Br).	HBr.
,, on charcoal with Na_2CO_3.	Dark brown infusible mass, reddish brown incrustation.	Cd.
,, ,, ,, ,, $Co(NO_3)_2$.	——	——
,, ,, platinum wire.	——	——

Wet Examination for Base.

Added HCl.	No pp.	Absence of Grp. I.
,, H_2S.	Yellow pp., insoluble in $(NH_4)_2S$ and $(NH_4)_2CO_3$, but soluble in HNO_3.	**Cd.**
,, NH_4OH.	White pp., soluble in excess.	,,

Examination for Acid.

Added $BaCl_2$.	——	——
,, $AgNO_3$.	Yellowish white pp., difficultly soluble in NH_4OH.	**HBr.**
Heated substance with MnO_2 and H_2SO_4.	Brown vapour of Br_2.	,,
Chlorine water added, and solution shaken up with CS_2.	Brown solution of Br_2. in CS_2 sinks to the bottom.	,,

Base, CdO. **Acid, HBr.**

[Cadmium Bromide, $CdBr_2$.]

5. Orange-red,* amorphous powder, insoluble in water, soluble in strong HCl, with decomposition.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in dry tube.	—	—
,, with HCl.	Smell of H_2S } Confirmed by blackening of lead } acetate paper.	A sulphide.
,, H_2SO_4.	,, ,, }	,,
,, on charcoal with Na_2CO_3.	Residue gives black stain on silver coin.	Sulphur compound.
,, on platinum wire.	Violet flame with white fumes.	K, Pb, As, Sb, Bi.

Wet Examination for Bases.

Added HCl (to dissolve).	Soluble in the concentrated acid with evolution [of H_2S.	Absence of Grp. I.
,, H_2S to diluted solution.	Orange-red pp.	Sb.
Treated pp. with $(NH_4)_2S$.	Soluble.	,,
,, ,, ,, $(NH_4)_2CO_3$.	Insoluble.	,,
In Marsh's apparatus.	Black stain, insoluble in NaClO.	,,

Examination for Acid.

The preliminary experiments conclusively show presence of sulphide, which was confirmed by the evolution of H_2S on boiling with HCl.

Base, Sb_2O_3. **Acid, H_2S.**

[Antimony Sulphide, Sb_2S_3.]

* The colour of the native sulphide which is not soluble in cold HCl is dark grey.

6. A White Crystalline Substance. Soluble in Water.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in a dry tube.	Water given off, acid reaction.	——
,, with HCl.	——	——
,, ,, H_2SO_4.	——	——
Heated on charcoal before B.P. flame.	Residue white, luminous, neutral to test paper.	Al_2O_3 [SiO_2].
Added cobalt nitrate to residue, and ignited.	A blue mass is left.	Al_2O_3 [SiO_2, &c.].
Added Na_2CO_3 to a portion, and ignited on charcoal.	Residue stains silver coin.	S compound.

Wet Examination for Base.

Added HCl.	No pp.	Absence of Grp. I.
,, H_2S.	,, ,,	,, ,, II.
To a fresh portion of solution added NH_4Cl and NH_4OH.	A white pp.	**Al.**
Confirmed Al by adding NaOH to a fresh portion of solution until the pp. at first formed is redissolved.	On adding NH_4Cl the pp. is again thrown down.	**Al.**

Examination for Acid.

Added $BaCl_2$.	A white pp. insoluble in HCl.	**H_2SO_4.**

Base, Al_2O_3. **Acid, H_2SO_4.**

[Aluminium Sulphate, $Al_2(SO_4)_3$.]

7. White amorphous powder. Insoluble in water, soluble in HCl.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in dry bulb-tube.	Becomes yellow-white when cool.	Zn.
,, with HCl.	Dissolves with slight effervescence.	CO_2 (*traces*).
,, ,, conc. H_2SO_4.	——	——
,, on charcoal with Na_2CO_3.	Yellow when hot, white when cold.	Zn.
,, ,, ,, ,, $Co(NO_3)_2$.	Heated mass becomes green.	Zn.
,, ,, platinum wire.	Reddish flame.	Trace Ca (?).

Wet Examination for Base.

Added HCl (as solvent).	——	Absence of Grp. I.
,, H_2S.	——	,, ,, II.
,, NH_4Cl, NH_4OH.	——	,, ,, III.
,, ,, ,, $(NH_4)_2S$.	White pp., insoluble in acetic acid.	Zn.
,, NaOH.	White gelatinous pp., soluble in excess.	,,

Examination for Acid.

Boiled portion of solid substance with Na_2CO_3, filtered, neutralized filtrate with HNO_3, and added		
$BaCl_2$.	——	——
$AgNO_3$.	——	——
$FeCl_3$.	——	——
Substance is *insoluble* in water		Absence of HNO_3 and $HClO_3$.
[No acid present.]		

Base, ZnO. [Zinc Oxide.]

8. White amorphous powder. Insoluble in water and acids.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in dry bulb tube.	—	—
,, with HCl.	—	—
,, ,, H_2SO_4.	—	—
,, on charcoal with Na_2CO_3	Residue stains silver coin.	S. compounds.
,, on platinum wire.	Yellowish-green flame.	B

Wet Examination for Base.

Fused original substance in porcelain crucible with ten times its weight of Na_2CO_3. Boiled fused mass in water, filtered, dissolved residue in HCl and examined for Base

Added H_2S.	—	Absence of Grp. II.
,, NH_4Cl, NH_4OH.	—	,, ,, III.
,, ,, ,, $(NH_4)_2S$.	—	,, ,, IV.
,, ,, ,, $(NH_4)_2CO_3$.	White pp.	Ba, Sr, Ca.
,, $CaSO_4$.	Immediate white pp.	**Ba.**

Confirmed by Preliminary Examination.

Examination of Filtrate for Acid.

Neutralized with HNO_3.	—	—
Added $BaCl_2$.	White pp. insoluble in HCl.	H_2SO_4.

Confirmed by Preliminary Examination and by insolubility of salt.

Base, BaO. **[Barium Sulphate, $BaSO_4$].** **Acid, H_2SO_4.**

9. White amorphous powder. Slightly soluble in water. Neutral.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in dry bulb tube.	——	——
,, with HCl.	——	——
,, ,, H_2SO_4.	——	——
,, on charcoal with Na_2CO_3.	——	——
Placed residue on silver coin.	Dark stain on coin.	Sulphur compounds.
Heated on charcoal.	——	——
,, ,, ,, with $Co(NO_3)_2$.	——	——
,, ,, platinum wire.	Red flame (traces of Sr flame).	Ca, Sr.

Wet Examination for Base.

Added HCl.	No pp.	Absence of Grp. I.
,, H_2S.	,, ,,	,, ,, II.
,, NH_4Cl, NH_4OH.	,, ,,	,, ,, III.
,, ,, ,, $(NH_4)_2S$.	,, ,,	,, ,, IV.
,, ,, ,, $(NH_4)_2CO_3$.	White pp.	Ba, Sr, Ca.
,, $CaSO_4$.	No pp.	**Ca.**
,, $(NH_4)_2C_2O_4$.	White pp.	,,

Examination for Acid.

Added $BaCl_2$.	White pp., insoluble in HCl.	**H_2SO_4.**

Confirmed by Preliminary Examination.

Base, CaO. **Acid, H_2SO_4.**

[Calcium Sulphate, $CaSO_4$.]

10. White crystalline substance. Soluble in water.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in a dry tube.	Substance gives off water.	——
,, with HCl.	——	——
,, ,, H_2SO_4.	——	——
,, on charcoal before the B.P. flame.	A white mass, highly luminous under the B. P., alkaline to test paper.	BaO, SrO, CaO, or MgO.
Added a drop of cobalt nitrate to the infusible residue, and ignited strongly.	A pink mass is left.	MgO.
Heated on charcoal with Na_2CO_3, and placed residue on silver coin.	Dark stain on coin.	Sulphur compound.

Wet Examination for Base.

Added HCl.	No pp.	Absence of Grp. I.
,, H_2S.	,,	,, ,, II.
,, NH_4Cl and NH_4OH.	,,	,, ,, III.
,, ,, ,, and $(NH_4)_2S$.	,,	,, ,, IV.
,, ,, ,, $(NH_4)_2CO_3$.	,,	,, ,, V.
To a portion of the solution added AmCl, NH_4OH, and Na_2HPO_4.	A white crystalline pp.	**Mg.**

Examination for Acid.

Added $BaCl_2$.	A white pp., insoluble in HCl.	**H_2SO_4.**

Base, MgO. **Acid, H_2SO_4.**

[Magnesium Sulphate, $MgSO_4$].

11. White crystalline. Soluble in water.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in a dry tube.	Substance sublimes and gives off NH_3.	NH_4 salt.
,, with HCl.	—	—
,, ,, H_2SO_4.	—	—

Wet Examination for Base.

Added HCl.	No pp.	Absence of Grp. I.
,, H_2S.	,, ,,	,, ,, II.
,, NH_4Cl, NH_4OH.	,, ,,	,, ,, III.
,, ,, ,, and $(NH_4)_2S$.	,, ,,	,, ,, IV.
,, ,, ,, ,, $(NH_4)_2CO_3$.	,, ,,	,, ,, V.
,, KOH to the original solution and heated.	Odour of ammonia.	NH_4.

Examination for Acid.

Added $BaCl_2$.	A white pp., soluble in HCl.	—
,, $AgNO_3$ to another portion.	A yellow pp., soluble in HNO_3.	H_3PO_4. [Arsenic has been proved absent.]
To another portion added NH_4Cl, NH_4HO, and $MgSO_4$.	A white crystalline pp.	H_3PO_4.

Base, NH_4OH. **Acid, H_3PO_4.**

[Ammonium Hydrogen Phosphate, $(NH_4)_2HPO_4$.]

12. White granular powder. Soluble in water. Solution alkaline.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in a dry tube.	—	—
,, with HCl.	Strong effervescence.	A carbonate.
Passed the gas evolved on adding HCl through clear lime-water.	The lime-water becomes turbid.	,, ,,
Heated on charcoal before the B.P.	Fuses and sinks into the charcoal.	An alkali.
Heated in the Bunsen flame on platinum wire after addition of HCl.	A golden yellow flame.	Sodium.

Wet Examination for Base.

Added HCl until reaction was strongly acid. Boiled until CO_2 was no longer evolved.	No pp.	Absence of Grp. I.
To a portion of solution added H_2S.	,, ,,	,, ,, II.
To another portion added NH_4Cl and NH_4OH.	,, ,,	,, ,, III.
Added $(NH_4)_2S$ to last solution.	,, ,,	,, ,, IV.
,, $(NH_4)_2CO_3$.	,, ,,	,, ,, V.
To another portion added NH_4Cl, NH_4OH, and Na_2HPO_4.	,, ,,	Absence of Mg.
Evaporated remainder of solution to small bulk and added $PtCl_4$.	,, ,,	,, ,, K, NH_4.
Boiled a portion of the powder with KOH.	No odour of NH_3.	,, ,, NH_4.

Base, Na_2O. **Acid, H_2CO_3.**

[Sodium Carbonate, Na_2CO_3.]

13. White, crystalline. Soluble in water. Neutral.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in dry bulb-tube.	Fuses.	Alkaline salt.
,, with HCl.	SO_2 evolved, and solution yellow with separated sulphur.	$H_2S_2O_3$.
,, ,, H_2SO_4.	H_2S, and finally SO_2 evolved, sulphur [yellow] separated.	,, [H_2S.]
,, on charcoal with Na_2CO_3.	Residue gives black stain on silver coin.	Compounds of S.
,, ,, platinum wire.	Yellow flame.	Na.

Wet Examination for Base.

Added HCl.	SO_2 evolved on heating, and S precipitated	[$H_2S_2O_3$.] Absence of Grp. I.
,, H_2S.*	No pp.	Absence of Grp. II.
,, NH_4Cl, NH_4OH.	,, ,,	,, ,, ,, III.
,, ,, ,, and $(NH_4)_2S$.	,, ,,	,, ,, ,, IV.
,, ,, ,, ,, $(NH_4)_2CO_3$.	,, ,,	,, ,, ,, V.
,, ,, ,, ,, $NaHPO_4$.	,, ,,	,, ,, Mg.
Boiled solution with NaOH.	NH_3 *not* given off.	,, ,, NH_4.
Added $PtCl_4$ and alcohol.	No pp.	,, ,, K.

Metal present must be **Sodium**, confirmed by preliminary examination.

Examination for Acid.

Added $BaCl_2$.	White pp. soluble in HCl; solution slowly precipitates sulphur.	$H_2S_2O_3$.
,, $AgNO_3$.	White pp. soluble in excess of solution; on adding excess of $AgNO_3$ and gently heating, pp. becomes black with Ag_2S.	$H_2S_2O_3$.

Confirmed by preliminary examination.

Base, NaOH. **[Sodium Thiosulphate, $Na_2S_2O_3$.]** **Acid, $H_2S_2O_3$.**

* If a white pp. is obtained, it is S, due to action of SO_2, liberated by HCl on SH_2.

14. Yellow, crystalline. Soluble in water.

Preliminary Examination.

Experiment.	*Observation.*	*Inference.*
Heated in a dry tube.	——	——
,, with HCl.	Solution darkens.	Chromate.
Heated on charcoal before blowpipe flame.	Residue coloured.	——
Fused a portion of residue in borax bead.	A green bead in both flames.	Cr.
Heated another portion in flame on platinum wire.	Violet-coloured flame.	K.

Wet Examination for Base.

Added HCl.	Solution darkens. No pp.	A chromate. Absence of Grp. I.
To the above added H_2SO_3.	Solution turns green.	A chromate.
Boiled off excess of H_2SO_3, and to a portion of solution added H_2S.	No pp.	Absence of Grp. II.
To remainder of solution added NH_4Cl and NH_4OH.	A dull green pp.	Cr.
Filtered, and to small portions of filtrate added (i.) $(NH_4)_2S$, (ii.) $(NH_4)_2CO_3$, and (iii.) Na_2HPO_4.	No pp.	Absence of Grps. IV. and V., and of Mg.
Evaporated to dryness main portion of filtrate, and ignited until fumes ceased to come off.		
Took up residue with HCl, and added $PtCl_4$.	A yellow crystalline pp.	K.

Examination for Acid.

Added $BaCl_2$.	A yellow pp.	H_2CrO_4.

Base, K_2O. **Acid, H_2CrO_4.**

[Potassium Chromate, K_2CrO_4.]

APPENDIX I.

ATOMIC WEIGHT TABLE.

N.B.—The atomic weights in the following table are sufficiently accurate for the purposes of ordinary quantitative analysis.

Aluminium	Al	27	Lead	Pb	207
Antimony	Sb	120	Lithium	Li	7
Arsenic	As	75	Magnesium	Mg	24·3
Barium	Ba	137	Manganese	Mn	55
Bismuth	Bi	208	Mercury	Hg	200
Boron	B	11	Nickel	Ni	59
Bromine	Br	80	Nitrogen	N	14
Cadmium	Cd	112	Oxygen	O	16
Calcium	Ca	40	Phosphorus	P	31
Carbon	C	12	Platinum	Pt	195
Chlorine	Cl	35·5	Potassium	K	39
Chromium	Cr	52	Silicon	Si	28·5
Cobalt	Co	59	Silver	Ag	108
Copper	Cu	63·5	Sodium	Na	23
Fluorine	F	19	Strontium	Sr	87·5
Gold	Au	197	Sulphur	S	32
Hydrogen	H	1	Tin	Sn	119
Iodine	I	127	Zinc	Zn	65
Iron	Fe	56			

APPENDIX II.

Pressure of saturated aqueous vapour in millimetres of mercury (correct to 0·5 mm.).

Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.
5° C.	6·5 mm.	12° C.	10·5 mm.	19° C.	16·5 mm.
6	7	13	11	20	17·5
7	7·5	14	12	21	18·5
8	8	15	13	22	20
9	8·5	16	13·5	23	21
10	9	17	14·5	24	22
11	10	18	15·5	25	23·5

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	9	13	17	21	25	30	34	38
											4	8	12	16	20	24	28	32	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	12	15	19	23	27	31	35
											4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934	0969					3	7	11	14	18	21	25	28	32
							1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	7	10	13	16	20	23	26	30
											3	7	10	12	16	19	22	25	29
14	1461	1492	1523	1553							3	6	9	12	15	18	21	24	28
					1584	1614	1644	1673	1703	1732	3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875	1903					3	6	9	11	14	17	20	23	26
							1931	1959	1987	2014	3	5	8	11	14	16	19	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	14	16	19	22	24
											3	5	8	10	13	15	18	21	23
17	2304	2330	2355	2380	2405	2430					3	5	8	10	13	15	18	20	23
							2455	2480	2504	2529	2	5	7	10	12	15	17	19	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
											2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	3	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	3	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
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·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
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·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
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·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
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·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
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·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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